EFFORTS TOWARDS THE TOTAL SYNTHESIS OF VINIGROL

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Vinigrol is a novel diterpenoid isolated from a soil fungus, *Virgaria nigra*. From a medicinal point of view, vinigrol is of interest due to demonstrated antihypertensive and platelet-inhibiting properties. Additionally, it has been discovered to act as a tumor necrosis factor antagonist, halting the progression of AIDS-related complex to AIDS, and nerve stem cell proliferation promoter. Given the combination of a structurally unique, synthetically challenging carbon framework and potential pharmaceutical applications, our interest lies in the total synthesis of vinigrol. Synthetic strategies employing oxidative dearomatization and intramolecular Diels-Alder cycloaddition are used to access structures towards this intriguing molecule.

BIOGRAPHICAL SKETCH

Jason George Maxwell Morton was born in Houston, Texas, on the evening of September 28, 1980, the son of George R. and Kathleen E. Morton. From an early age he was indoctrinated in the belief that a Ph. D. was the natural endpoint of schooling, and has moved inexorably toward that end for what will probably be a good third of his lifetime. His family having moved to South Carolina, he attended 1st through 8th grades at Our Lady of Peace School in North Augusta, where his mother still teaches. It was there that Jason first began to love science, supported in particular by a science teacher Mrs. Carol Roach, who let him ask all sorts of questions and throw class off into interesting tangents.

Elementary education was followed by two years at Aquinas High School, located across the Savannah River in Augusta, Georgia. It was here where Jason would be introduced to chemistry through another wonderful teacher, Mrs. Searle – hard but fair, high schools need more teachers like Mrs. Searle. Jason's final two years of high school were spent at the South Carolina Governor's School for Science and Mathematics. As the name would imply, there were lots of science classes offered there. And again, fate would have it that another phenomenal chemistry teacher, Dr. Kurt Wagner, would cement Jason's opinion that, in the end, he should like to be a chemist someday. And own a tree farm.

Attending the Honor's College at the University of South Carolina, Jason spent much of his time as an undergraduate researcher in the lab of Prof. Uwe H. F. Bunz, a tall German man who once remarked in a concerned fashion, "Jason, you look stressed, you need more sex." In this supportive environment, and in a building with large windows, Jason worked with Matt Laskoski in synthesizing organometallic dehydroannulenes.

Having always wished to see New England, and erroneously believing New York to be a part of it, Jason began his graduate career at Cornell University in the Fall of 2003. There he joined the lab of Jón Njarðarson, a new assistant professor from Iceland who bore many conflicting political views which would provoke many enlivening debates. I'll be seeing about that whole socialized medicine thing when I'm in Canada. Biking to school in rain, shine, and snow, Jason has loved his time in Ithaca – "10 square miles surrounded by reality" – though he wishes the architects of S. T. Olin Laboratory had realized that graduate students would enjoy windows measuring larger than a mere 14.5 inches across. Now, having reached the end of his formal education, Jason dreams of 15 acres, a goat, and some ducks.

“What fun is it being cool if you can’t wear a sombrero?”

– Calvin and Hobbes

ACKNOWLEDGMENTS

Thanks to my parents for their love and support through the years.

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LIST OF ABBREVIATIONS

AIBN	1,1′-Azobis(cyclohexanecarbonitrile)
B-Br-9-BBN	*B*-Bromo-9-borabicyclo[3.3.1]nonane
CSA	(+/–)-Camphor-10-sulfonic acid
DIBAL-H	Diisobutylaluminum hydride
DMF	*N,N*-Dimethylformamide
B-I-9-BBN	*B*-Iodo-9-borabicyclo[3.3.1]nonane
HFIP	1,1,1,3,3,3-hexafluoroisopropanol
HMPA	Hexamethylphosphoramide
LTA	Lead tetraacetate, $Pb(OAc)_4$
MOM	Methoxymethyl
PIDA	Phenyliodine(III) diacetate, $PhI(OAc)_2$
PIFA	Phenyliodine(III) bis(trifluoroacetate), $PhI(COCF_3)_2$
PPTS	Pyridinium *p*-toluenesulfonate
RCM	Ring closing metathesis
RT	Room temperature
TBS	*t*-Butyldimethylsilyl
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
THP	Tetrahydropyranyl
TMEDA	*N,N,N',N'*-Tetramethylethylenediamine
TMS	Trimethylsilyl

PREFACE

Vinigrol is a diterpenoid isolated from a soil fungus, *Virgaria nigra*, found at the foot of Mount Aso in Japan.[1,2] Its structure was determined by chemical derivitization, NMR and mass spectrometry, and X-ray crystallography,[3] and noticeably bears resemblance to the bicyclo[5.3.1]undecane-containing taxanes. However, in vinigrol there exist two such superimposable [5.3.1] ring systems, formally giving it a tricyclo[4.4.4.0]-tetradecane skeleton, a framework unique to this particular molecule. From a medicinal point of view, vinigrol is of interest due to demonstrated antihypertensive and platelet-inhibiting properties.[4] Additionally, it has been discovered to act as a tumor necrosis factor antagonist, halting the progression of AIDS-related complex to AIDS,[5] and nerve stem cell proliferation promoter.[6] Given the combination of a structurally unique, synthetically challenging carbon framework and potential pharmaceutical applications, it is of no surprise that several research groups have published reports towards the synthesis of vinigrol. Yet despite work spanning more than 15 years from at least 9 independent laboratories, a total synthesis of this molecule has not been realized.

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Chapter 1

Prior Art

1.1 Perspectives of vinigrol

Given its complicated nature and the limitations of condensing a three-dimensional reality onto a two-dimensional surface, the drawn structure of vinigrol lends itself to numerous representations. Figure 1.1 shows six of these perspectives, chosen at times by various groups to best fit and illustrate the logic of their respective retrosynthetic analyses. In the Figures that follow, structure **1.5** will be used as a common form so that direct comparisons between routes can be made more easily.

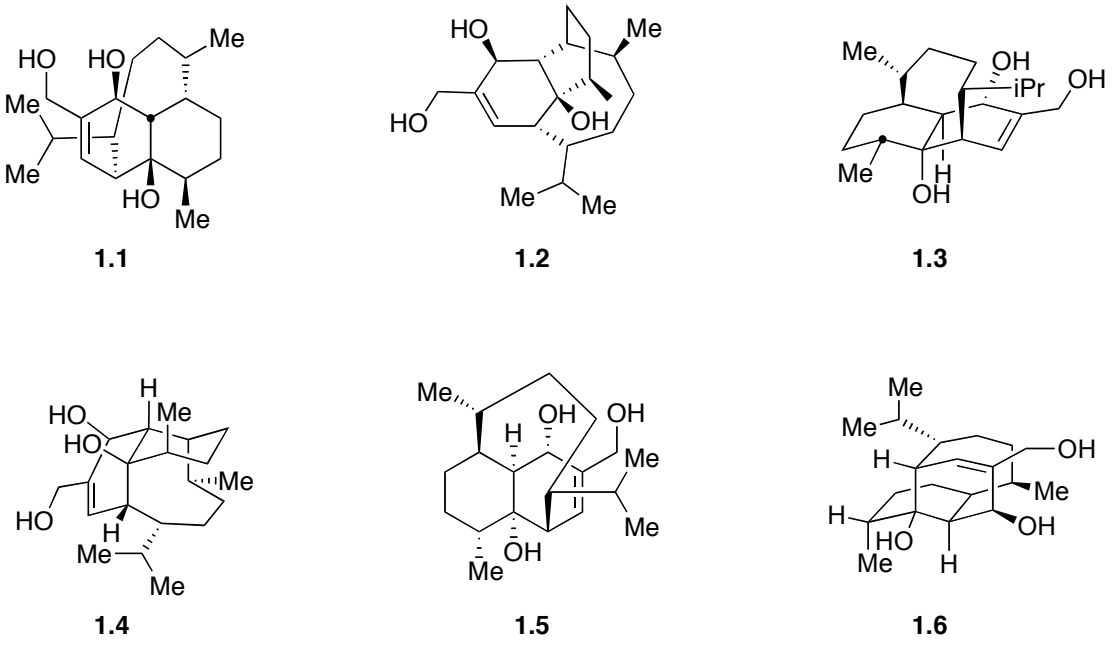

Figure 1.1. Six perspectives of vinigrol.

1.2 Published Work[1]

Two of the earliest studies towards vinigrol were conducted in the labs of Goverdhan Mehta[2] and F. Matsuda,[3] whose respective strategies are shown in Figures 1.2 and 1.3. In the Mehta lab, oxy-Cope rearrangement of a decalin framework was used to construct the bicyclo[5.3.1]undecane ring system present in both vinigrol and

paclitaxel. This system is very lightly functionalized, and to the best of our knowledge no further advances towards vinigrol were made.

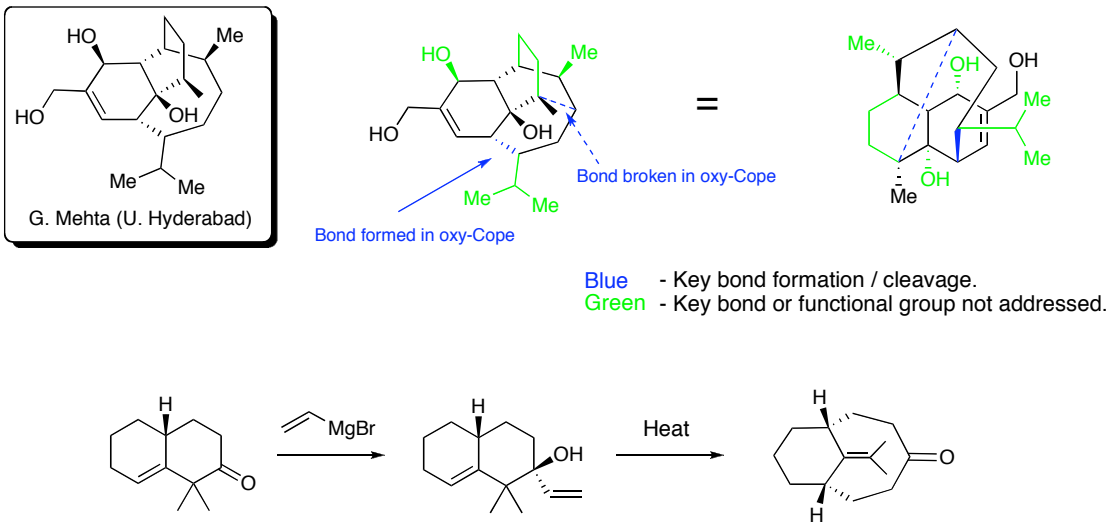

Figure 1.2. Summary of the Mehta route – oxy-Cope rearrangement for [5.3.1] bicyclic system.

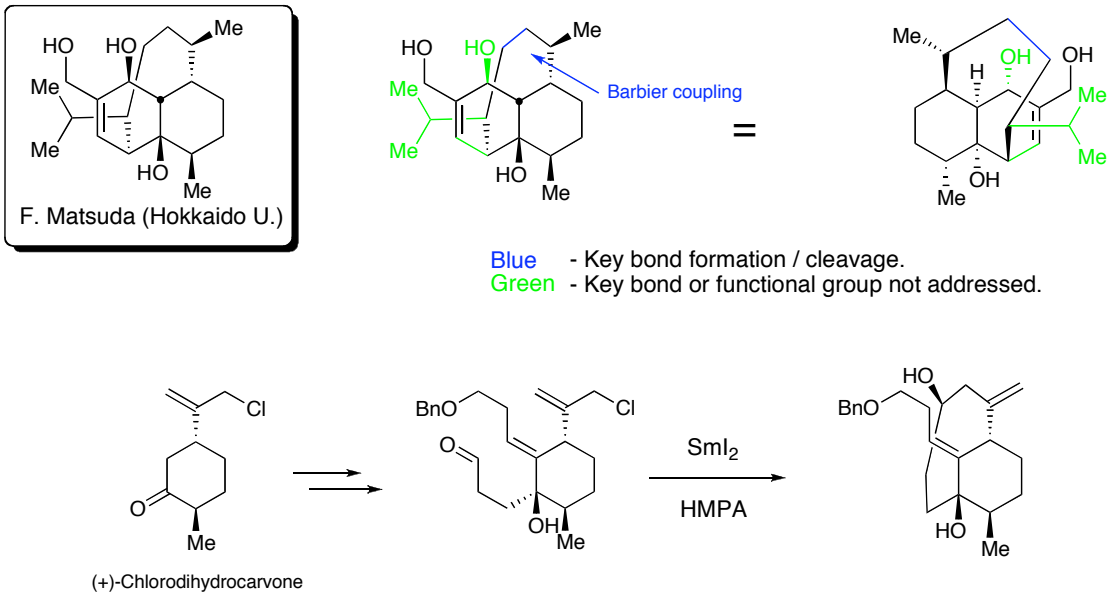

Figure 1.3. Summary of the Matsuda route – SmI_2 ring closure for [5.3.1] ring system.

Similarly, Matsuda *et al.* also reported a strategy for construction of the bicyclo[5.3.1]undecane core. The chiral-pool reagent carvone was derivatized by known methods, after which SmI_2-mediated Barbier coupling afforded a bicyclic system substantially more functionalized than that of Mehta. While further work was published[4] on an SmI_2-mediated closing to afford solely the *cis*-decalin ring system, no additional progress in either case has been reported.

One of the more imaginative approaches towards vinigrol has been that of Louis Barriault and co-workers, illustrated in Figure 1.4.[5] Viewing the *cis*-decalin system of vinigrol in chair-like form, they utilized a previously-disclosed[6] tandem oxy-Cope/Claisen/Alder ene rearrangement to generate the decalin ring system. Notably, the rearrangement cascade is only viable with terminal allylic alcohols.
Other work aimed at closing the eight-membered ring by Claisen rearrangement, ring closing metathesis, or McMurry coupling was unsuccessful.[7]

Indeed, this inability to "buckle" the tether in the endgame is also seen in the Paquette group's efforts towards vinigrol (Figure 1.5).[8] In this case, a bicyclo-[2.2.2]octane is opened to the *cis*-decalin *via* an oxy-Cope rearrangement. Numerous strategies – ring closing metathesis, pinacol coupling, McMurry coupling, direct nucleophilic substitution, ring contractions – to connect the four carbon tether proved unsuccessful.

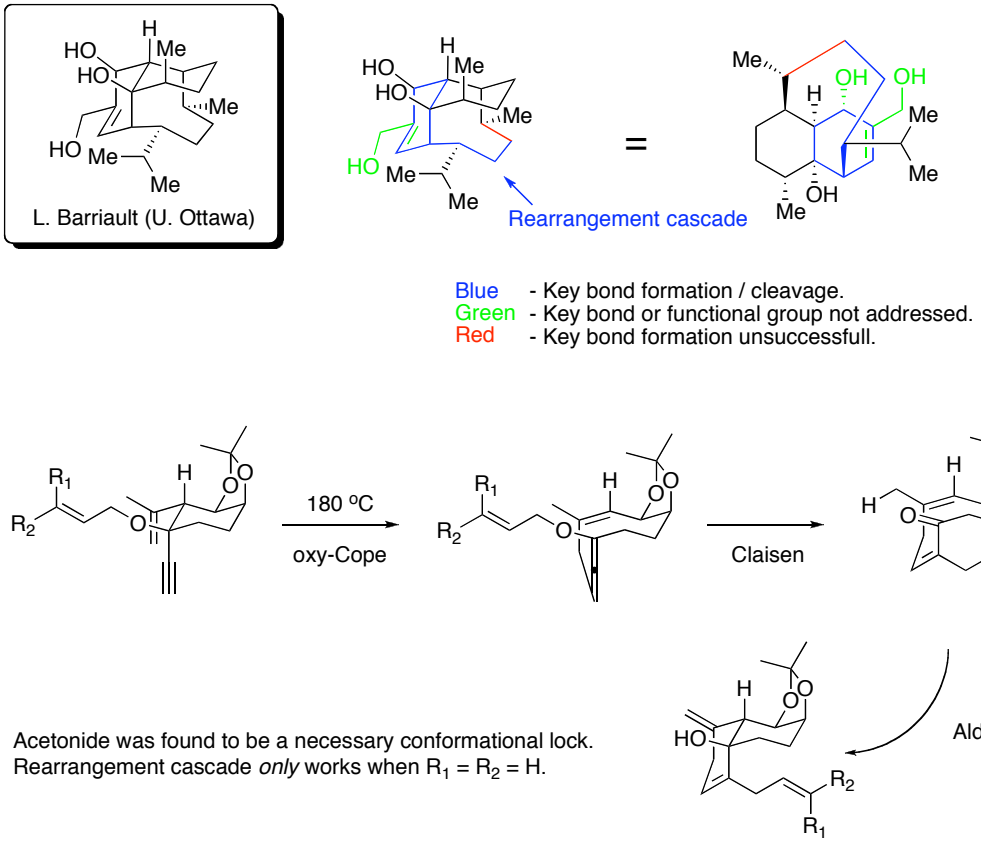

Figure 1.4. Summary of the Barriault route – [3,3] rearrangement cascade for *cis* decalin; attempts to "buckle" the eight-membered ring.

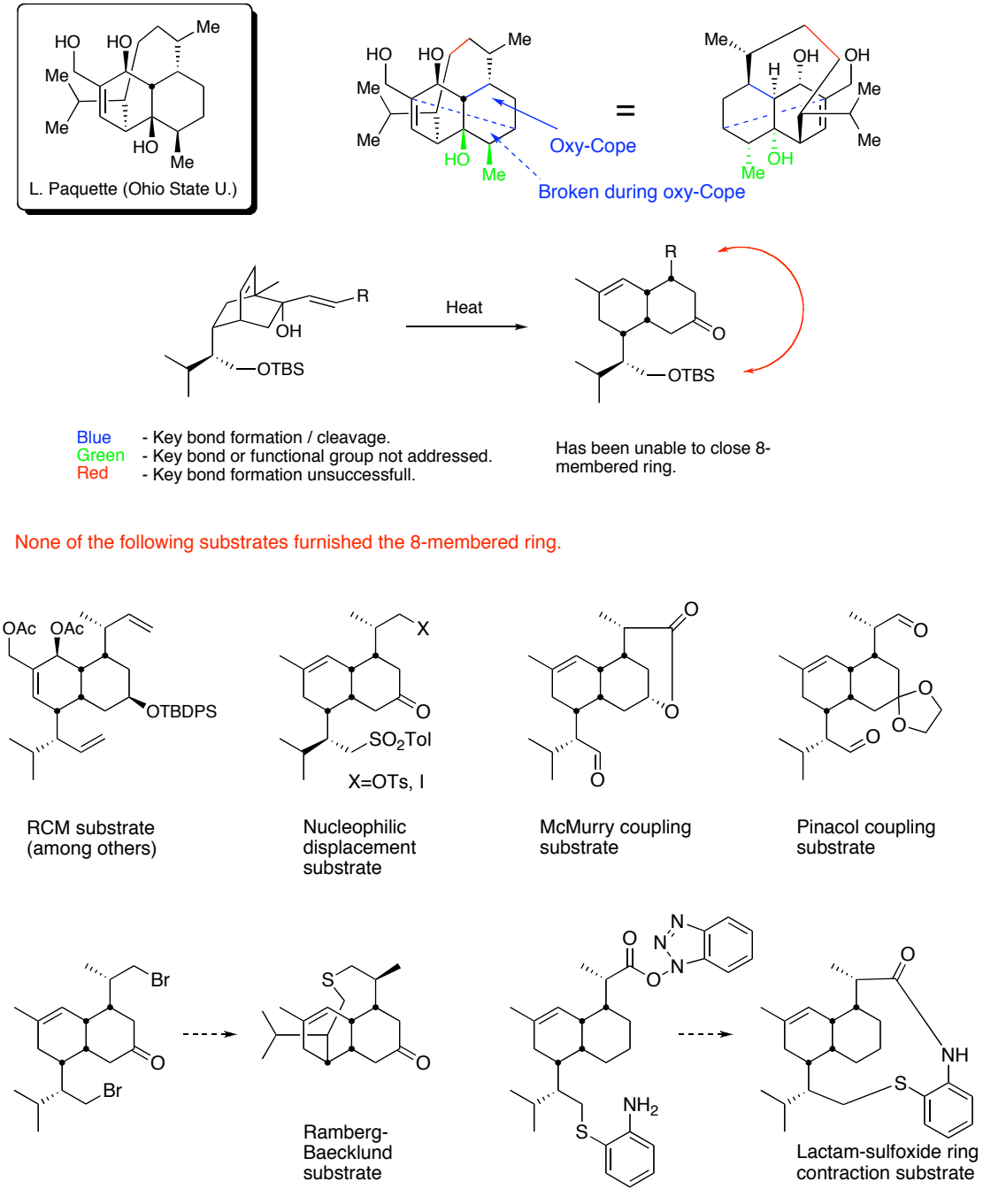

Figure 1.5. Summary of the Paquette route – oxy-Cope for construction of *cis*-decalin core; attempts to "buckle" the eight-membered ring.

Steven Goodman and E.J. Corey attempted formation of the *cis*-decalin system through a tethered Diels-Alder cycloaddition (Figure 7).[9] A Grob fragmentation was planned to later unveil the eight-membered ring as having been part of this tether. Unfortunately, and despite massive effort, no Diels-Alder product was ever observed.

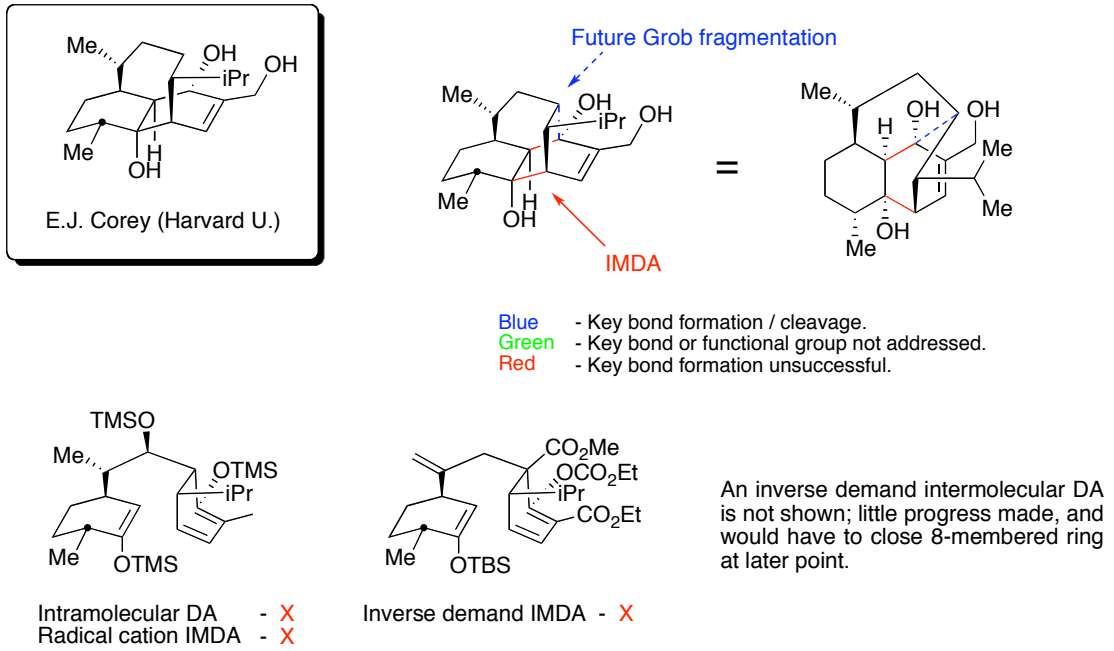

Figure 1.6. Summary of the Corey route – attempted IMDA for *cis*-decalin; ring cleavage for the cyclooctane ring.

With one of the most advanced precursors to date, the group of Issam Hanna has completed both the cyclooctane and *cis*-decalin units of vinigrol (Figure 1.7).[10] Beginning from an intermolecular Diels-Alder, elaboration of the resultant tricycle leads to the illustrated triene. Anionic oxy-Cope rearrangement occurs in 72% yield to give the complete carbocyclic core of vinigrol. Note that the rearrangement only takes place with the unsaturated isopropenyl group; isopropyl in either the *E* or *Z* conformation leads only to recovery of starting material or decomposition. Although the methyl stereochemistry is incorrect, reduction of the ketone followed by

elimination and hydrogenation afforded a 2:3 mixture of it as the desired *R* stereocenter. Incorporation of the critical tertiary oxygen is also feasible. However, despite being tantalizingly close, no publication concerning a complete synthesis has yet come forth.

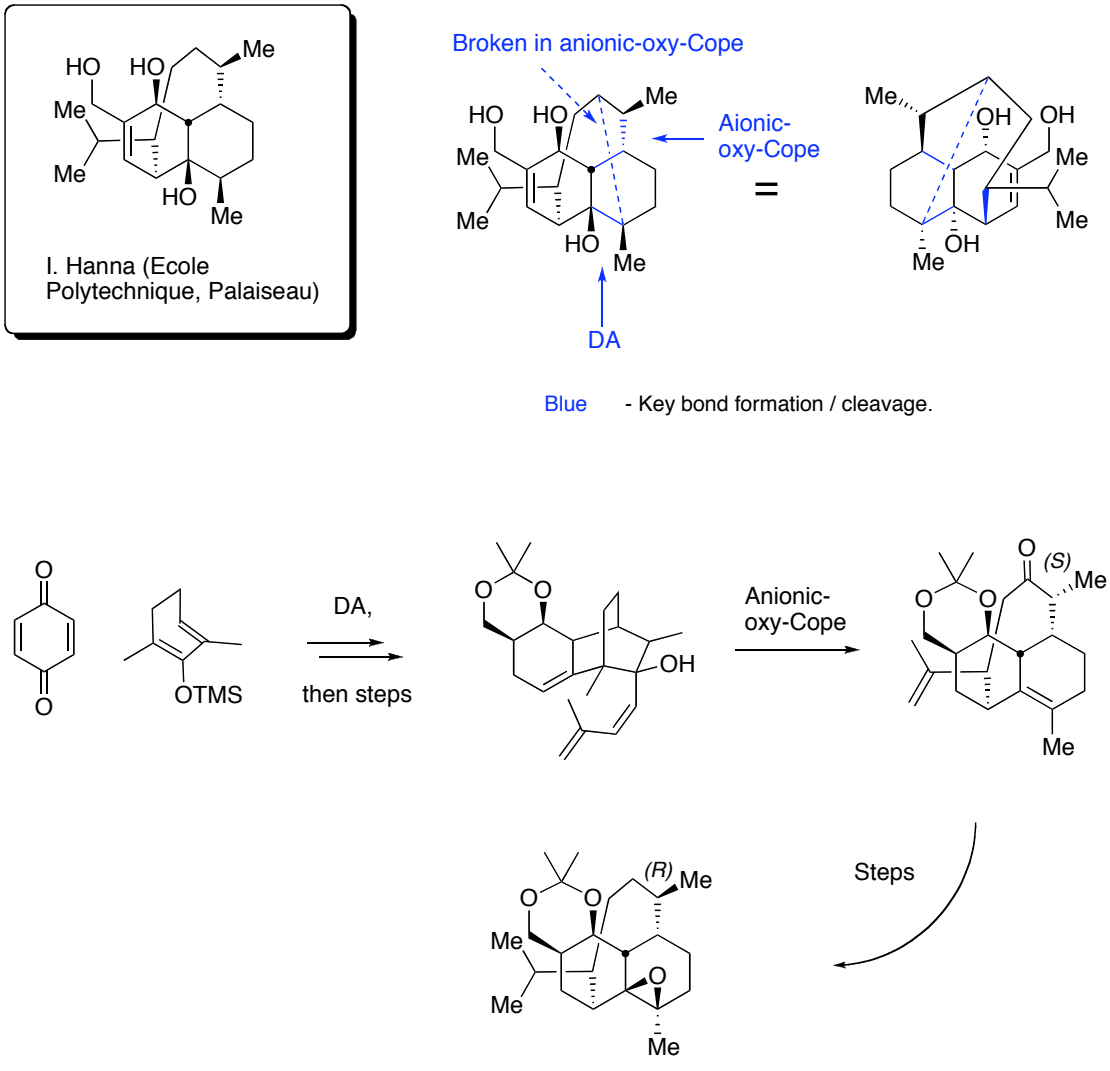

Figure 1.7. Summary of the Hanna route – Diels-Alder cycloaddition for *cis*-decalin, anionic oxy-Cope to close the eight-membered ring.

The Fallis group at the University of Ottawa has explored a route towards vinigrol that encompasses two Diels-Alder cycloadditions (Figure 1.8).[11] The first utilizes Lewis acid catalysis and principles of self-assembly to generate a functionalized core. After elaboration, a second Diels-Alder cycloaddition, intramolecular in nature, simultaneously forms the *cis*-decalin and fused cyclooctane ring systems.

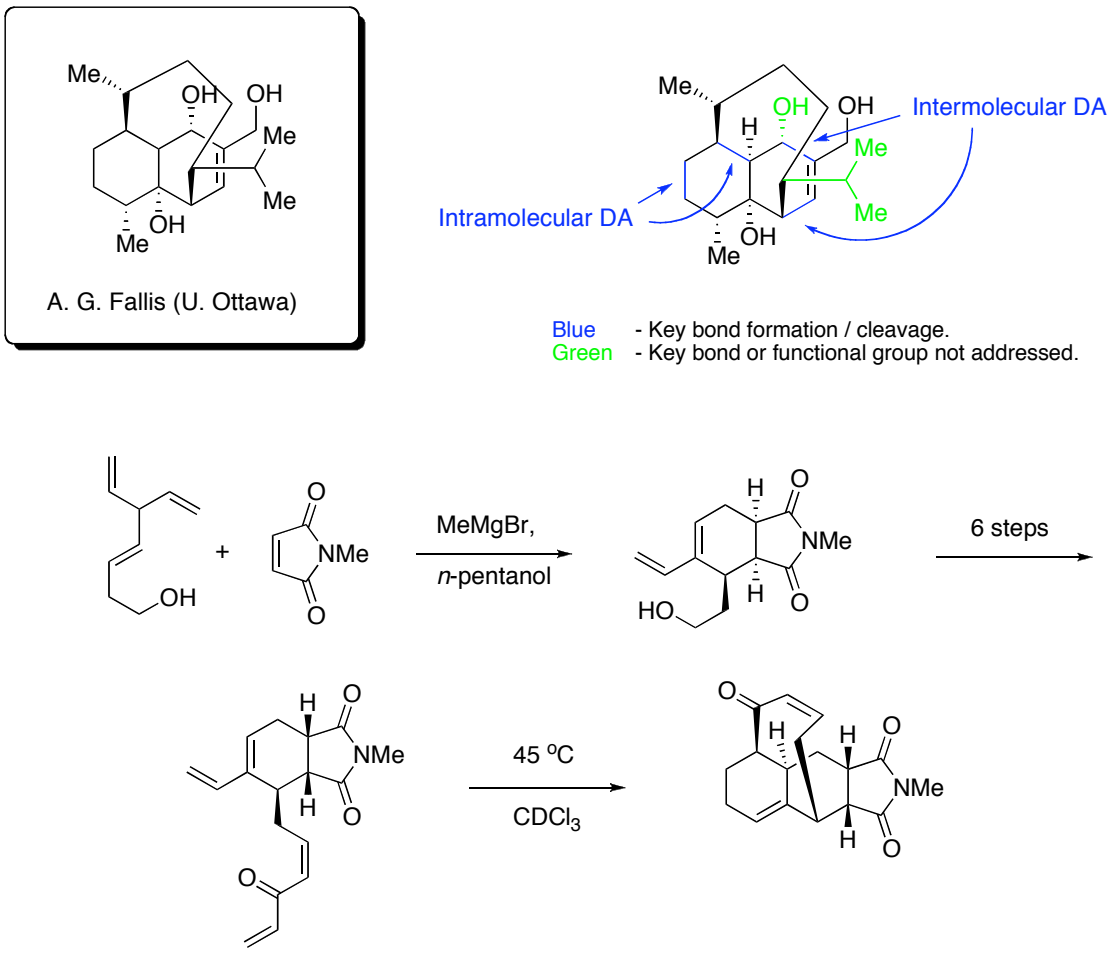

Figure 1.8. Summary of the Fallis route – Diels-Alder cycloadditions for key rings.

Finally, the Baran group has also utilized an intramolecular Diels-Alder strategy (Figure 1.9),[12] one which bears similarity to both the Corey and Fallis routes. An initial intermolecular Diels-Alder cycloaddition provides a bicyclo[2.2.2]octane skeleton which is elaborated to the triene, then engaged in an intramolecular cycloaddition to afford the core of vinigrol. Grob fragmentation, as originally envisioned by the Corey group, is indeed shown successful in "unmasking" the 4-membered tether of the cyclooctane ring.

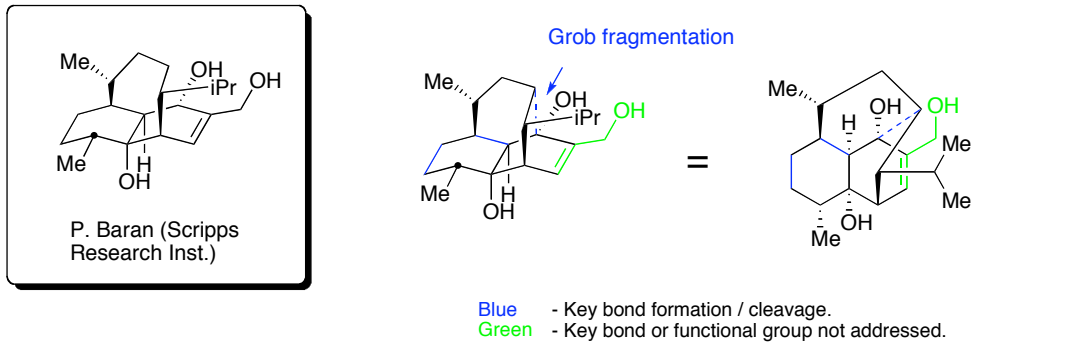

Figure 1.9. Summary of the Baran route – Diels-Alder cycloaddition and Grob fragmentations for core.

1.3 Conclusions

The preceding attempts towards vinigrol suggest that formation of the cyclooctane moiety in vinigrol cannot proceed after the *cis*-decalin core is complete (evident in the Barriault and Paquette routes). Rather, a strategy whereby both are formed simultaneously (the Fallis route) or the cyclooctane is present as a latent ring to be opened by rearrangement or carbon-carbon bond fragmentation (Hanna, Corey, and Baran routes) must be employed. Also, judging from what has not been shown by the Hanna and Baran groups, it might also be inferred that installation of the tertiary alcohol in the endgame would also prove quite difficult.

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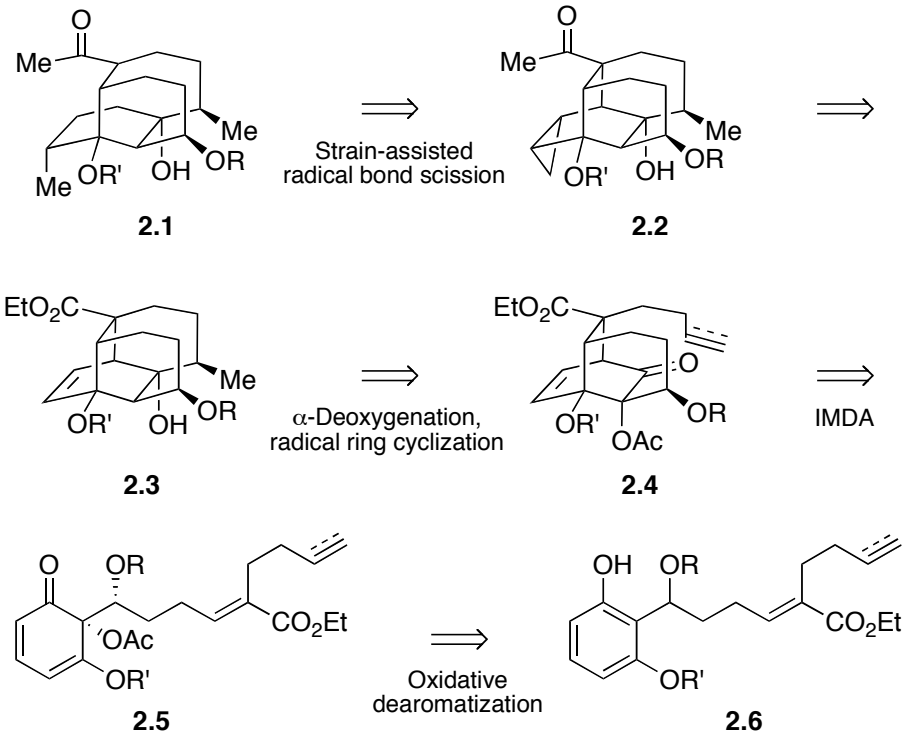
Chapter 2:

Initial Efforts: the Wessely Oxidative Dearomatization

2.1 Retrosynthetic Strategy

Our initial strategy for constructing an advanced vinigrol precursor (Scheme 2.1) consisted of four key operations. As it has been well-established that endgame closure of the eight-membered ring is infeasible,[1] it is our belief that selective bond cleavage of a bicyclo[2.2.2]octane system such as **2.2** will "unravel" a latent cyclooctane. Functional group manipulation then leads back to **2.3**, which we envision being generated from a 6-*exo*-trig or 6-*exo*-dig ring closure protocol of **2.4**. We imagine this bicyclic structure being produced in turn by the intramolecular Diels-Alder cycloaddition of a diene-containing *o*-benzoquinol **2.5**, itself generated via oxidative dearomatization of a suitably substituted phenol **2.6**.



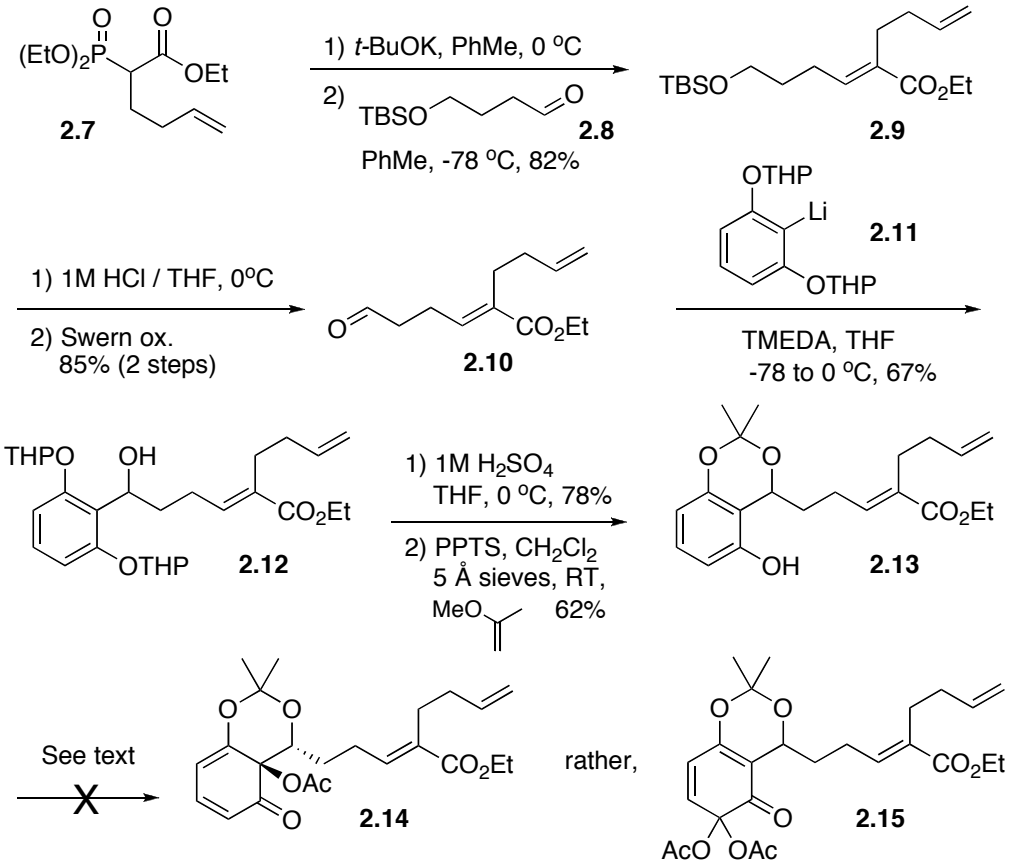
2.1 **2.2** **2.3** **2.4** **2.5** **2.6**

Scheme 2.1. Retrosynthesis of vinigrol

2.2 Synthetic Efforts

We initially focused on construction of the phenol **2.13** (Scheme 2.2) in the belief that, during oxidative dearomatization, the intramolecular acetonide tether would affect nucleophilic trapping from the opposite face as the large dienophile-bearing sidechain. Furthermore, this acetonide would bring the dienophile into the proximity of the *o*-benzoquinol ring, facilitating the Diels-Alder cycloaddition. Towards this goal, a *E*-selective Horner-Wadsworth-Emmons protocol[2] between phosphonate **2.7**[3] and aldehyde **2.8**[4] generated the tribustituted olefin **2.9**. Removal of the silyl protecting group and oxidation to the aldehyde then gave **2.10**. Formation of the *ortho*-lithiated[5] resorcinol derivative **2.11**[6] and electrophilic trapping with **2.10** then provided the benzylic alcohol **2.12**. Careful deprotection to the unstable triol and acetonide formation gave the desired **2.13**, and we were ready to attempt the first key step of our synthetic plan.

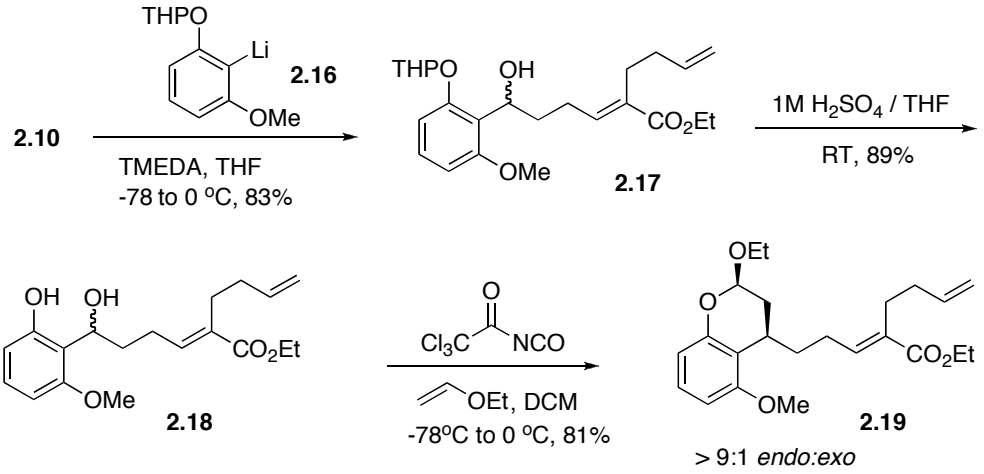
While the mechanism of oxidative dearomatization is dependent largely on the oxidant and conditions used, the Wessely oxidation,[7] employing $Pb(OAc)_4$, generally provides selectivity for nucleophilic incorporation of acetate at the most electron-rich site *ortho* to the phenol. We were thus disappointed to find that this reaction with **2.13** gave no detectable quinol (**2.14**), but rather the undesired and readily hydrolyzed masked quinol **2.15** along with small amounts of its *para* isomer. Efforts with other oxidants – $Pb(OAc)_4/BF_3$-Et_2O,[8] PIDA or PIFA,[9] benzeneseleninic anhydride,[10] and Cu(II)/morpholine/O_2[11] – were also unsuccessful in generating **2.14**.[12]



Scheme 2.2. First attempts at oxidative dearomatization.

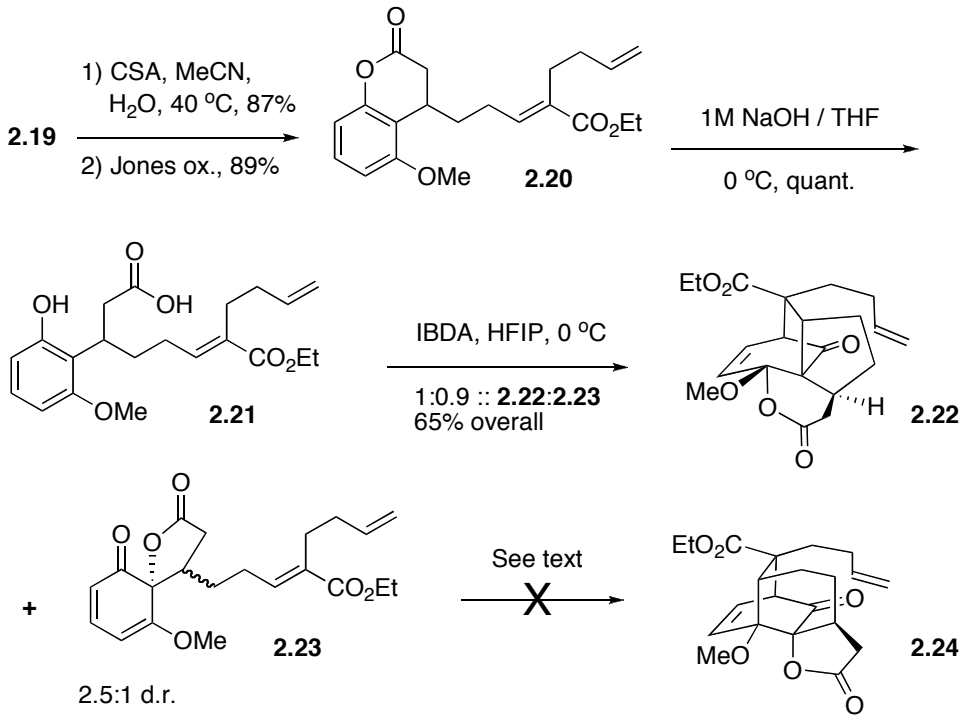
This failure in site selectivity led us to pursue a path (Scheme **2.3**) in which use of an intramolecular nucleophile would enforce attack at the proper position. A carbamate was chosen in the belief that it would behave analogous to an amide, where the carbonyl oxygen rather than the amide nitrogen is known act as nucleophile during oxidative dearomatization.[13] Beginning with aldehyde **2.10**, a similar nucleophilic addition with the *ortho*-lithiated resorcinol derivative **2.16** formed the benzylic alcohol **2.17**. While it was possible to form various carbamates from this alcohol, successive deprotection of the THP moiety inevitably led to elimination through an *ortho*-quinone methide pathway and subsequent decomposition. In an effort to put this proclivity to good use, however, it was discovered that treatment of the diol **2.18** with

trichloroacetylisocyanate[14] in ethyl vinyl ether and CH_2Cl_2 as co-solvents efficiently led to the hetero Diels-Alder adduct **2.19** in one pot with good yield.[5a,15] Indeed, this appears to be a quite mild means for the *in situ* formation of *ortho*-quinone methides.[16]



Scheme 2.3. *o*-Quinone methide-mediated hetero Diels-Alder.

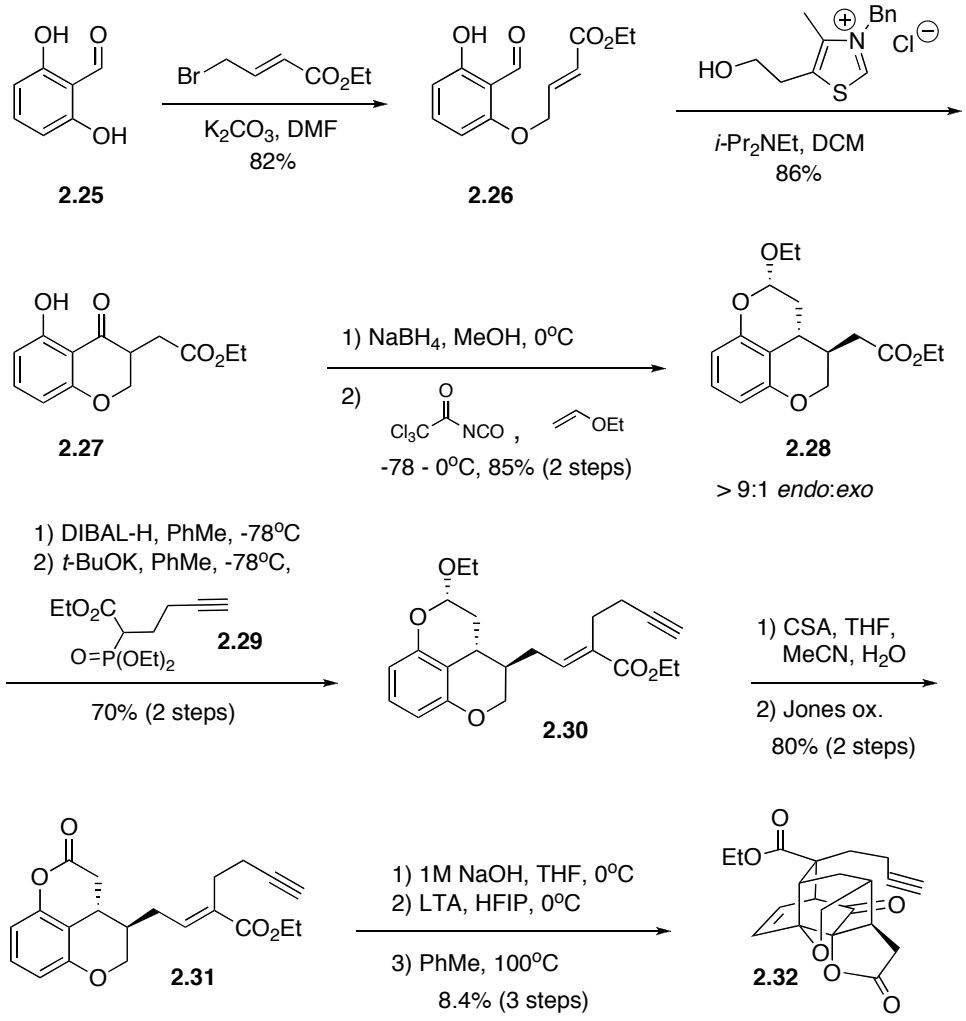
Continuing with our efforts towards vinigrol (Scheme 2.4), hydrolysis of the acetal **2.19** with camphorsulfonic acid and subsequent Jones oxidation realized lactone **2.20**, which could be readily opened under alkaline conditions to the free acid **2.21**. Optimized oxidative dearomatization of **2.21** with iodobenzene diacetate (IBDA) in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), however, resulted in three products: the unanticipated bicyclic adduct **2.22** and a nearly equal combined amount of the two spirobenzoquinol diastereomers **2.23** (2.5:1 *d.r.*). The bicyclic **2.22**, whose structure was confirmed by X-ray crystallography of a pivaloate derivative, probably results from a polar cationic [5+2] cycloaddition made possible by the electron donating character of the methoxy substituent.[17] While separation of the spirobenzoquinol diastereomers **2.23** proved intractable, heating the mixture at reflux in benzene or toluene failed to afford any Diels-Alder adduct (**2.24**), with more forcing or Lewis acidic conditions leading only to decomposition.



Scheme 2.4. Formation of a [5+2] cationic cyclization product.

Altering the dienophile electronics might have enabled the Diels-Alder cycloaddition of **2.23**, but this would have no effect on the poor diastereoselectivity[18] of the oxidative dearomatization and the formation of **2.22** as a major byproduct. We thus sought to synthesize a construct which would exhibit both a predetermined stereoselectivity in the oxidative dearomatization and a geometrical inhibition of the [5+2] adduct. To this end, the known benzaldehyde **2.25**[19] was monocrotonylated and engaged in an intramolecular Stetter reaction[20] to form the chromanone **2.27** (Scheme 2.5). Reduction with $NaBH_4$ led to the diol, after which use of our quinone methide-generating protocol yielded the adduct **2.28** with nearly complete facial diastereoselectivity (confirmed by NOESY NMR spectroscopy). Reduction to the aldehyde was accomplished with DIBAL-H, after which Horner-Wadsworth-Emmons olefination was employed to generate **2.30**. Deprotection to the lactol and Jones

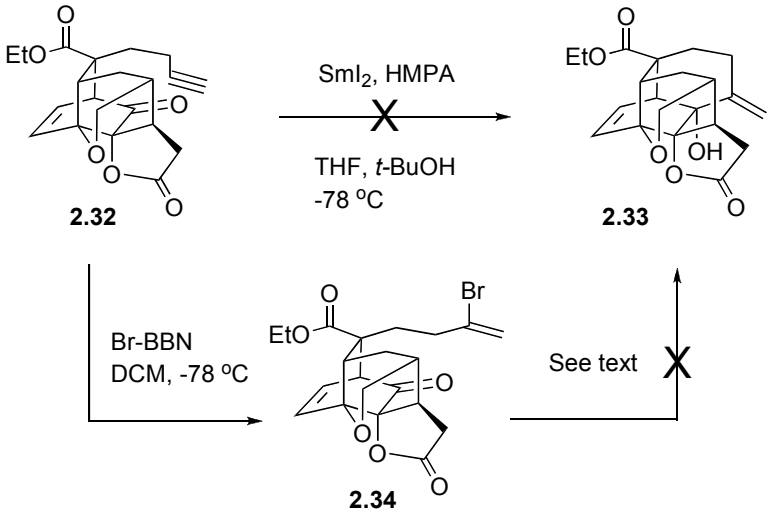
oxidation gave lactone **2.31**. While opening to the free acid was again facile, the oxidative dearomatization proceeded in exceedingly poor yield despite extensive testing of oxidants, solvents, and temperature conditions. Reasons for this difficulty are unclear. Gratifyingly, however, the intramolecular Diels-Alder proceeded well, allowing us to indeed access the desired bicyclic structure **2.32**.[21]



Scheme 2.5. Successful Diels-Alder cycloaddition.

With **2.32** in hand, it was then incumbent to affect closure of the posterior six-membered ring. We had initially envisioned a radical cyclization for this purpose

(Scheme **2.6**); however, employment of SmI_2 proved unsuccessful, giving only a mixture of unidentified compounds. Changing tack, treatment of **2.32** with *B*-Br-9-BBN[22] gave the vinyl bromide **2.34** with which we hoped to employ a "top-down" cyclization approach. Unfortunately, efforts at transmetallation employing *t*-BuLi[23] and *n*-Bu_2CuLi[24] were unsuccessful in forming identifiable products, while Nozaki-Hiyama-Kishi[25] coupling conditions likewise failed to close the posterior six-membered ring. The difficulty might lie in the extreme steric crowding of the compact and rigid bicyclic ring systems preventing the incoming nucleophile from approaching the carbonyl at the requisite Bürgi-Dunitz trajectory.[26]



Scheme 2.6. Attempted closure of the back ring.

Although we were disappointed in our inability to close this last ring, it was about this time when we discovered that a different dearomatization, the Adler-Becker oxidation, could be employed successfully on a derivative of the Stetter product **2.27**. Given the synthetically untenable yields for the transformation of **2.31** to the bicyclic adduct **2.32**, we began to explore this new route, the subject of the following chapter.

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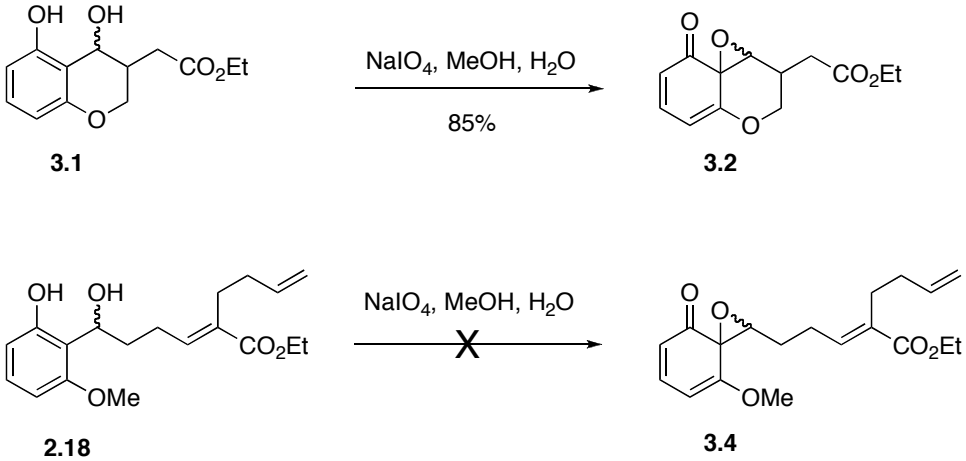
Chapter 3

Further Efforts: the Adler-Becker Oxidative Dearomatization

3.1 Fortuitous Development

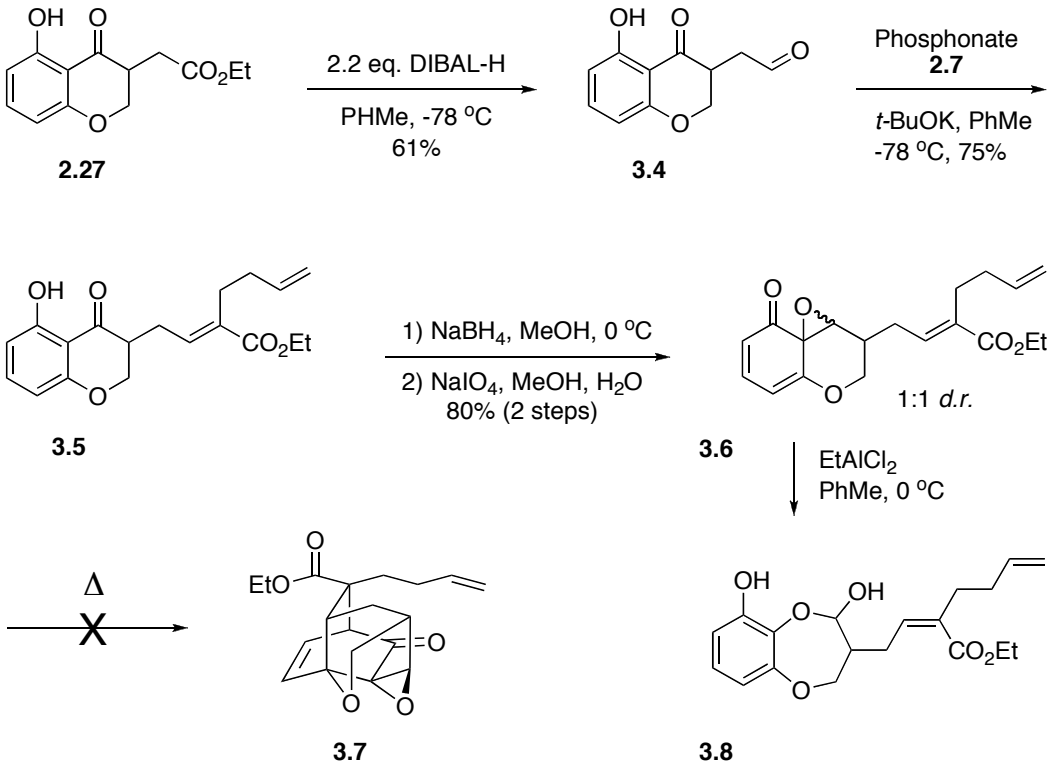
First reported in 1971, the Adler-Becker reaction is the periodate-mediated oxidative dearomatization of salicylalcohols to *spiro*-epoxydienones.[1] The majority of synthetic applications utilizing this reaction do so with primary benzyl alcohols.[2] Only a handful of reports[3] in the literature utilize secondary alcohols for this purpose, indicating that oxidation of such subtrates is far more challenging. A notable exception is the oxidation of reduced tetralone derivatives, which have been most famously utilized for the total synthesis of the natural product triptolide.[4] Indeed, in our hands the acyclic diol **2.18** was unsuccessful in forming spiroepoxide **3.3** when treated with $NaIO_4$ in $MeOH/H_2O$. (Scheme 3.1). Conversely, treatment of diol **3.1** (generated by simple $NaBH_4$ reduction of **2.27**) with $NaIO_4$ immediately turns the reaction mixture yellow, a characteristic indicator that a benzoquinol is being formed. We were quite pleased to find that spectroscopic analysis of the reaction product confirmed the *spiro*-epoxy **3.2**. With an additional oxidative dearomatization protocol open to us, we began to explore a new pathway towards vinigrol.



Scheme 3.1. Initial Adler-Becker test reactions.

3.2 Synthetic Efforts

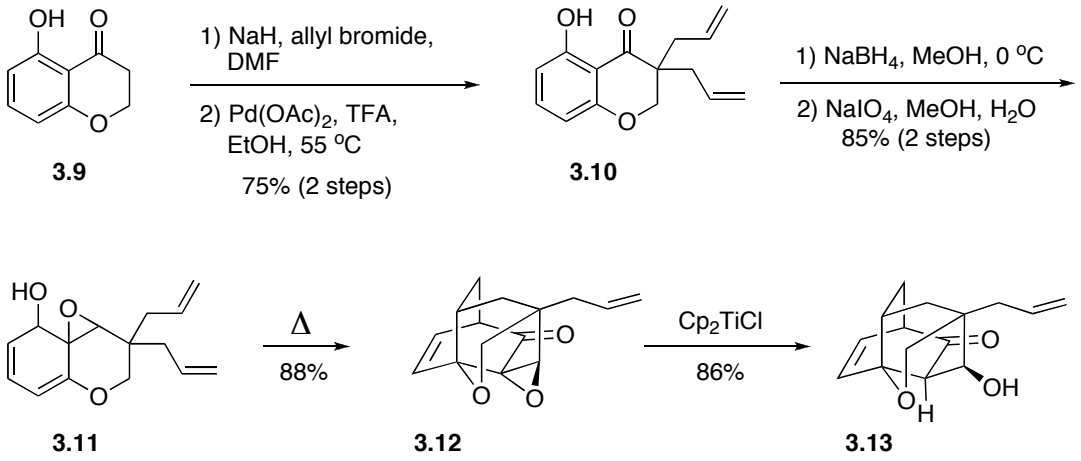
Our initial explorations took advantage of the previously-generated chromanone **2.27** from our Wessely oxidation efforts (see Chapter 2). Selective partial reduction to the aldehyde **3.4** could be accomplished with controlled addition of DIBAL-H in toluene at –78 °C (Scheme 3.2). Horner-Wadsworth-Emmons homologation[5] using phosphonate **2.7** then afforded enoate **3.5**. Ketone reduction with $NaBH_4$ provided an Adler-Becker oxidation substrate (1:1 *d.r.*) that dearomatized readily to **3.6** upon treatment with $NaIO_4$ in $MeOH/H_2O$. While we recognized that only one of the diastereomers is competent for the cycloadditions, disappointingly the desired intramolecular Diels-Alder product **3.7** was never generated. Mild heating



Scheme 3.2. Initial Adler-Becker route.

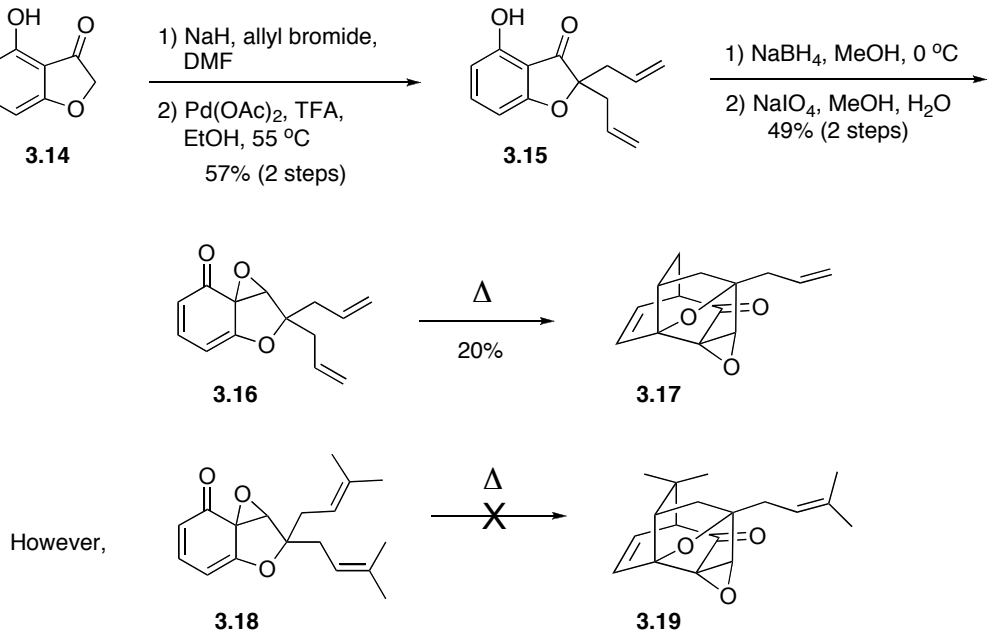
returned only starting material, with higher temperatures (>150 °C) leading only to decomposition. Attempts at low temperature, Lewis-acid-mediated Diels-Alder cycloadditions likewise failed in generating the desired bicycle. Rather, reaction with $EtAlCl_2$ at 0 °C led to the rearrangement product **3.8**. This in stark contrast with our previous Wessely oxidation results, wherein the oxidation reaction proved very challenging while the cycloaddition proceeded smoothly (Scheme 2.5).

Unsatisfied with this result, we regrouped to a simpler substrate in order to explore this approach further. Beginning from known chromanone **3.9**[6] (Scheme 3.3), exhaustive allylation was followed by deprotection to afford free phenol **3.10**. Reduction and Adler-Becker oxidation then yielded the desired dienone **3.11** in good yield. We were delighted to learn that, upon prolonged heating in toluene at 150 °C, the tetracyclic cycloadduct **3.12** was formed in excellent yield. Finally, Cp_2TiCl-mediated radical opening of the epoxide[7] gave the alcohol **3.13**. This simple model substrate contains much of the vinigrol pre-fragmentation core, with all of the challenging hydroxyl groups in their respective positions.



Scheme 3.3. A successful Diels-Alder cycloaddition.

Catalyzed by this success, and in parallel with our chromanone model studies, we argued that a smaller fused framework might bring the dienophile closer to the dienone and hence enable cycloaddition at temperatures low enough to preclude decomposition of our sensitize *spiro*-quinols. Models and our calculations suggested that such a *spiro*-dienone product (**3.16**) would bring the two cycloadduct component closer together, so a benzofuranone variant of the chromanone model system was chosen (Scheme 3.4).

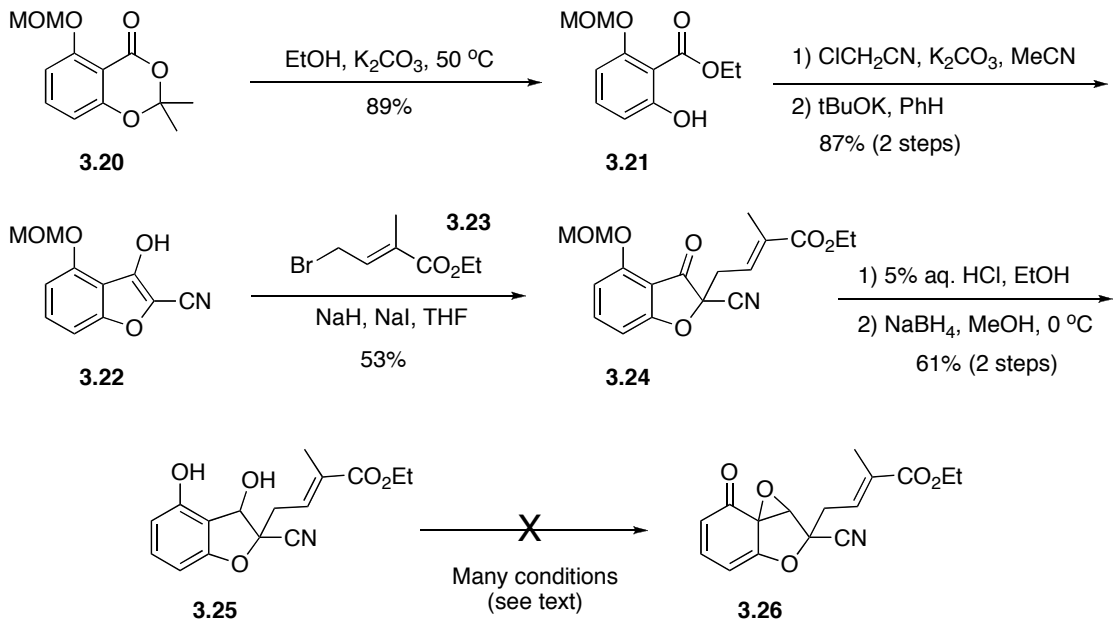


Scheme 3.4. The benzofuranone framework.

These studies utilized known benzofuranone **3.14**[8] as a starting point, which is readily accessed from commercially available 2,6-dihydroxyacetophenone. Ketone **3.15** was obtained as **3.10** before, by first exhaustively allylating and then selectively deallylating to the free phenol. This new structure is both more rigid and sterically congested than its predecessor, and this is reflected in a slower reduction and lower yielding Adler-Becker oxidation to **3.16**. Indeed, it proved difficult to "force" the oxidative dearomatization to completion, as oxidation back to the ketone became a

competing reaction. It thus proved more effective to partially convert to **3.16** and recover the remaining starting material. Careful heating of the dearomatized core afforded highly strained cycloadduct **3.17**, albeit in non-optimal yields. Again, we believe this is reflective of the highy strained nature of this product. In order to better assess the scope of this approach we also accessed prenylated core **3.18** using an identical synthetic approach. This tetraene resisted all attempts to cyclize to **3.19**, with decomposition occurring at elevated temperatures.

Having realized moderate success in both the oxidative dearomatization and subsequent Diels-Alder cycloaddition of **3.17**, we investigated this benzofuran framework further using more advanced synthetic components (Scheme 3.5). Transesterification of the known benzodioxanone **3.20**[9] with EtOH gave **3.21**. Alkylation of the free phenol with chloroacetonitrile and subsequent condensation then yielded the β-ketonitrile **3.22**. Keeping in mind the failure of the *bis*-prenyl **3.18** adduct to undergo Diels-Alder cycloaddition, we decided to use an electronically more matching enoate dienophile in this route. Selective *C*-alkylation with **3.23**[10] was thus used, affording **3.24**. Deprotection of the phenolic MOM group and reduction of the ketone set the stage for the critical dearomatization step. Unfortunately, diol **3.25** resisted all of our attempts to convert it to *spiro*-dienone **3.26**. Conditions attempted include: $NaIO_4$, $MeOH/H_2O$; $NaIO_4$, AcOH; $NaBiO_3$, AcOH; $Cu(CH_3CN)_4PF_6$, morpholine, DIEA, CH_2Cl_2, O_2; $CuCl_2$-morpholine, MeCN, MeOH, O_2; $CuCl_2$, pyridine, MeOH, O_2; $PhI(OAc)_2$, CF_3CH_2OH; H_5IO_6, MeOH; H_5IO_6, THF. No Adler-Becker product was ever observed in these reactions; when any reaction at all occurred it was reoxidation to the ketone.



Scheme 3.5. Difficulties in oxidative dearomatization.

In summary, despite this route being a dead end for our vinigrol campaign it does serve to highlight both the untapped synthetic potential of the Adler-Becker dearomatization in rapidly accessing complex structures and the need that exists for reactive, selective oxidizing agents for such processes.

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Chapter 4

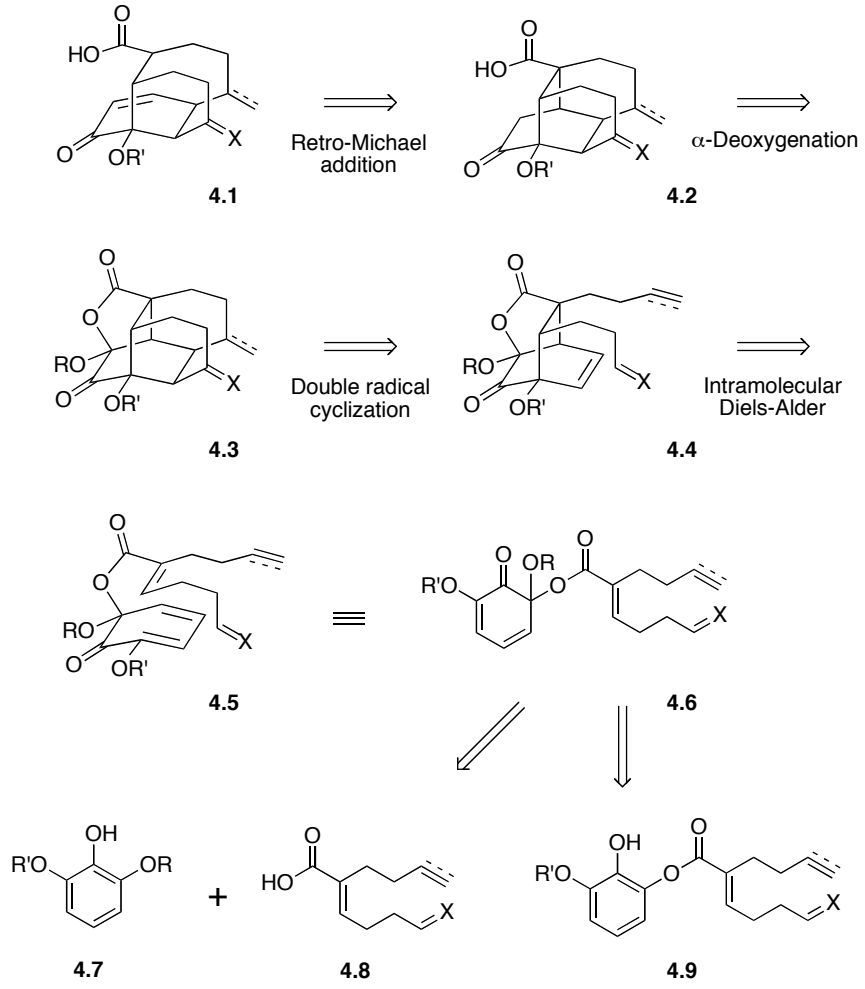
A Tandem Radical Cyclization Route

4.1 A New Retrosynthesis

Having encountered difficulties in utilizing the Adler-Becker oxidation for the synthesis of vinigrol's carbocyclic core, we began seeking a related yet more robust route that would prove successful in both the key oxidative dearomatization and intramolecular Diels-Alder cycloaddition steps. We thus developed the plan outlined in Scheme 4.1. Here, the core of vinigrol (**4.1**) is envisioned as accessible from a retro-Michael reaction of **4.2**. Double deoxygenation[1] then leads back to **4.3**, and tandem radical cyclization[2] to **4.4**. As far as we are aware, such a 6-*exo*/6-*exo* cascade would be unprecedented.[3,4,5,6] And here again we have a substrate accessible from the intramolecular Diels-Alder cycloaddition of a cyclohexa-2,4-dienone (**4.5**/**4.6**).

The masked *ortho*-benzoquinone **4.5**/**4.6** can be envisioned as proceeding from either of two oxidative dearomatizations. In the first case (involving **4.7**, **4.8**) the acid sidechain is used as the incoming nucleophile. This could be accomplished by performing a Wessely oxidation:[7] ligand exchange[8] with one or more of the acetates of $Pb(OAc)_4$ would provide a species which could directly transfer the desired acid during the oxidative dearomatization.[9] Although use of the allylic alcohol as nucleophile may also be envisioned, in practice we found that this precluded use of $Pb(OAc)_4$, while use of PIDA or PIFA led to poor intermolecular incorporation of the alcohol unless vast excesses of it were employed.[10] Given the hypothesized mechanism of PIDA and PIFA oxidative dearomatizations[11] – the nucleophile is not directly transferred from the reagent – this is not surprising. The second case, oxidative dearomatization of **4.9**, would be fraught with regioselectivity issues. Indeed, if R' were a simple ether we would expect oxidation to occur solely at this more electron rich site. With this in mind, we decided to pursue a route based on **4.7**/**4.8**, believing it would provide the greatest flexibility in altering the phenol ring and acid sidechain as needed.

We are quite happy that this newest retrosynthesis still utilizes the same four key reactions as before, namely: oxidative dearomatization, intramolecular Diels-Alder cycloaddition, radical cyclization, and strain-induced bond cleavage to "unmask" the latent cyclooctane. Aesthetically, then, the theme remains the same.

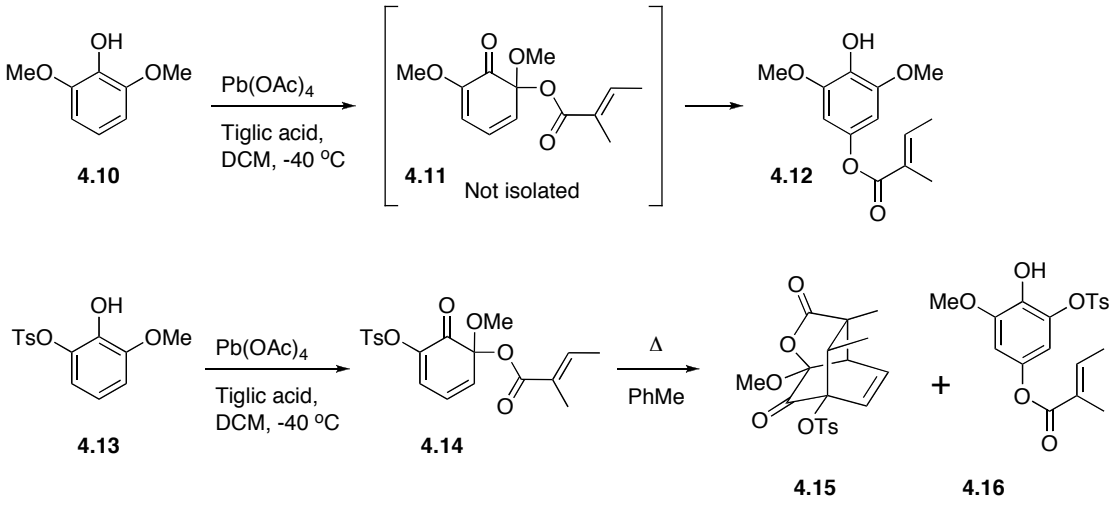


Scheme 4.1. Retrosynthesis for a tandem radical cyclization.

4.2 Attempted Tandem Radical Cyclization Route

We began by testing the feasibility of the oxidative dearomatization and subsequent Diels-Alder cycloaddition (Scheme 4.2). Hoping to use the commercially

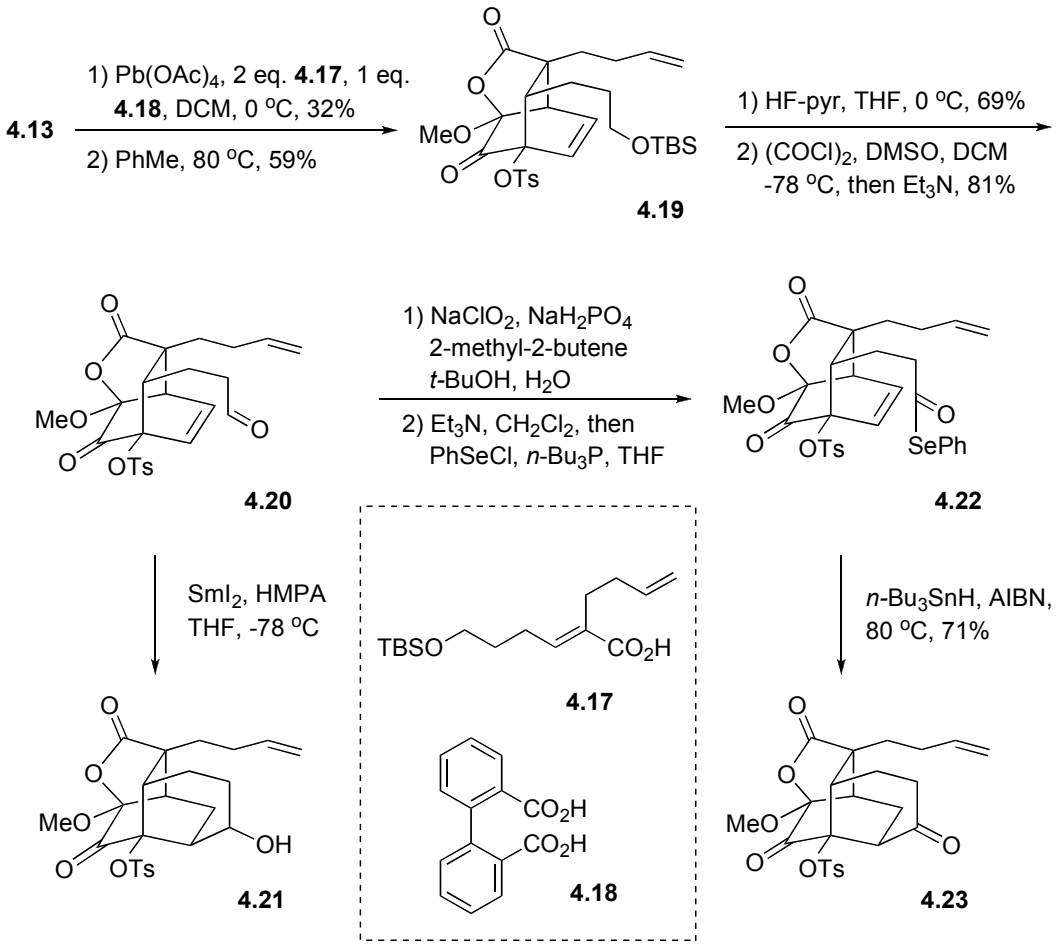
available 2,6-dimethoxyphenol (**4.10**), oxidation with tiglic acid provided not the desired **4.11** but rather the rearomatized **4.12**, accessed through a [3,3] acetate migration.[12] Brief efforts to block this shift by installing a bromine *para* to the phenol[13] were pursued, but the resultant products were unstable and decomposed when heated. A tosylated pyrogallol **4.13** was then synthesized in the belief that the withdrawing nature of the sulfonate ester would prevent or at least diminish any rearrangements. And indeed, we were excited when oxidation of this phenol with $Pb(OAc)_4$ in the presence of excess tiglic acid provided the desired ketal **4.14**. Heating this compound in toluene then led to the Diels-Alder adduct **4.15**, though now unfortunate amounts of the rearrangement product **4.16** (~1:0.3) were seen.



Scheme 4.2. Oxidative dearomatization / Diels-Alder feasibility study.

Buoyed by this success, we first utilized the acid **4.17** (Scheme 4.3) in our efforts, as it was easily accessible from the ester **2.9** used in our earlier routes. Oxidative dearomatization and Diels-Alder cycloaddition led to **4.19**, which although produced in low yields allowed for overall 66% recovery of the starting material acid **4.17**. Bicycle **4.19** could be desilylated and oxidized to the aldehyde **4.20** in good

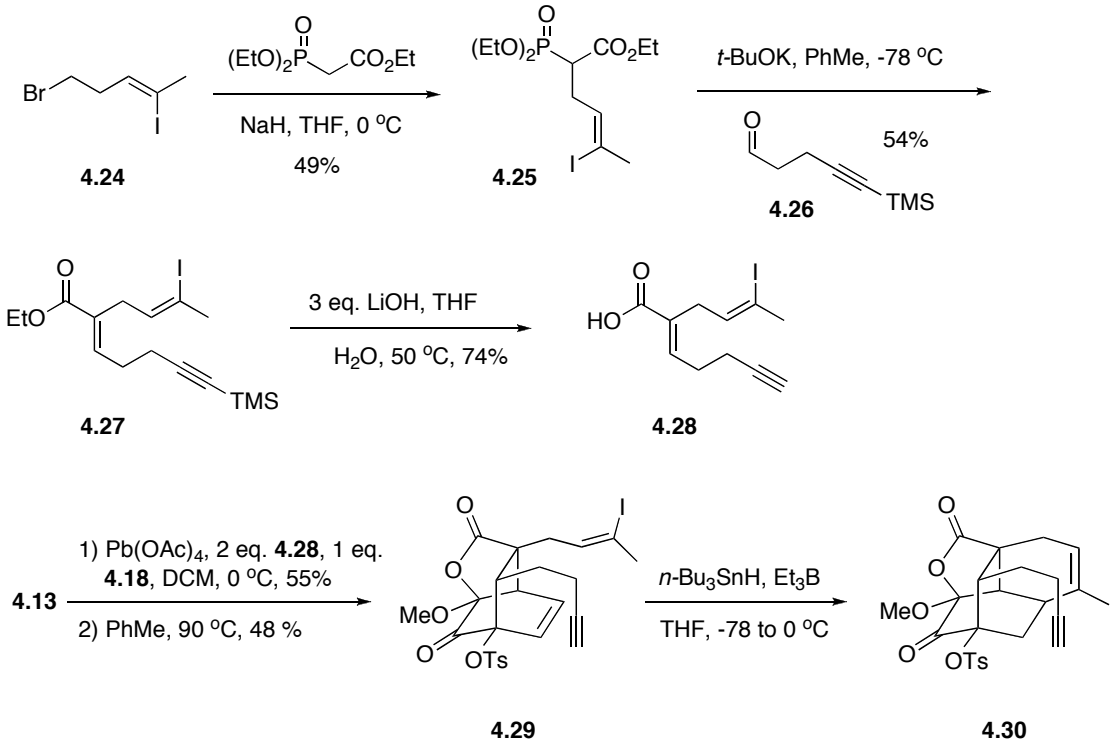
yield. Treatment of **4.20** with samarium(II) iodide[14] and HMPA in THF successfully led to a cyclized product, however one in which the back ring had not closed. This is evident from ^{1}H-NMR spectra clearly showing retention of the terminal olefin.



Scheme 4.3. Attempted front-to-back tandem radical cyclization.

It thus seems the 2° radical generated after the initial cyclization is quenched faster than it can "find" the alkene, which is not surprising given the compact nature of the system we are asking it to form. So to at least slightly minimize steric congestion we oxidized the aldehyde **4.20** to the acid, which could then be transformed to the acyl selenide **4.22**. Treatment of this species with *n*-Bu_3SnH and AIBN in refluxing benzene or C_6F_6 gives a planar acyl radical, but this again formed only the

monocyclized product. Efforts to initiate the cyclization with reagents exhibiting slower hydrogen donation – and hence slower quenching – were then pursued. In the event, however, $(TMS)_3SiH$ led to problems with hydrosilylation of the alkene, while *n*-Bu_3GeH proved unsuccessful in generating any cyclized product.



Scheme 4.4. Attempted back-to-front tandem radical cyclization.

Excited that we could successfully close one ring, it seemed a matter of fine-tuning the sidechains so as to minimize adverse steric interactions. We thus began the back-to-front cyclization strategy shown in Scheme 4.4. Generating the phosphonate **4.25** from allyation of triethylphosphonoacetate with known **4.24**[15], Horner-Wadworth-Emmons homologation[16] of aldehyde **4.26**[17] provides ester **4.27**. Hydrolysis of both the ester and silyl groups can be accomplished with lithium hydroxide, providing the acid **4.28**. Oxidative dearomatization and Diels-Alder

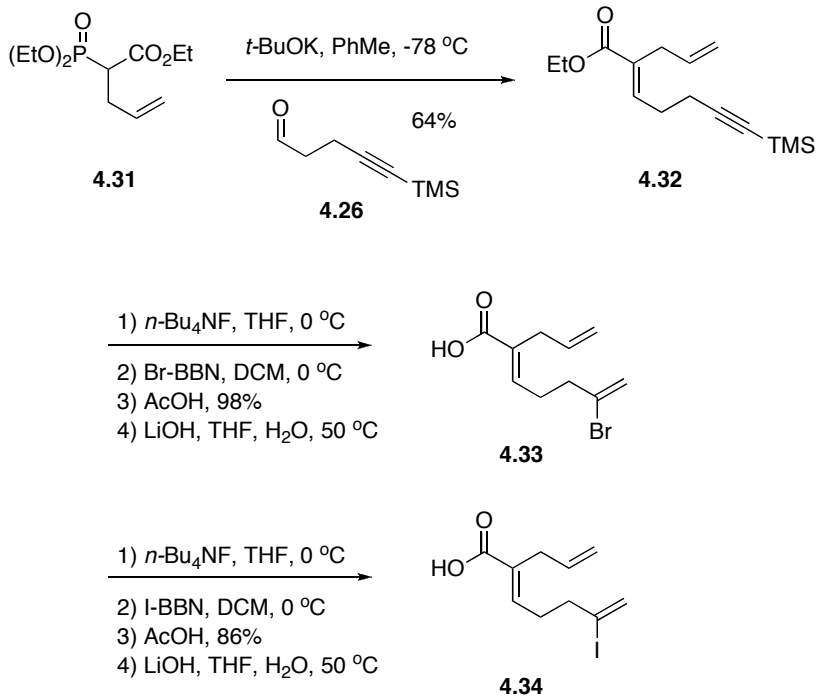
cycloaddition then gives the bicycle **4.29**, and we are ready to generate a vinyl radical. Note that the geometry of this vinyl iodide for radical cyclization is inconsequential;[18] however, by accessing the *Z*-olefin we have a substrate that is also suitable for a possible palladium-catalyzed cascade.[19]

Here we are attempting a 6-*exo*-trig/6-*exo*-dig double radical cyclization. Since the alkene is internal, the first cyclization will form a ring with only one methylene proton occupying space within the cage structure, hopefully minimizing any steric conflicts in forming the second ring. In the event, treatment of vinyl iodide **4.30** at low temperature with *n*-Bu_3SnH and Et_3B still only provided a monocyclized product **4.30**; no indication of characteristic *exo*-methylene protons in the ^{1}H-NMR spectra was ever observed. Again, the slower hydrogen donors $(TMS)_3SiH$ and *n*-Bu_3GeH were also employed. With the former, decomposition became a problem, perhaps because the resultant $(TMS)_3SiI$ can be expected to be highly oxophilic. Interestingly, the germanium hydride provided a product, not yet fully characterized, which shows definite closing of the rear ring but also loss of the tosyl group. This would suggest the unfortunate property that allowing the 2° radical too great of a lifetime adjacent to the tosyl group leads to its reductive elimination, this event being faster than the desired 6-*exo*-dig cyclization.

4.3 A Stepwise Route

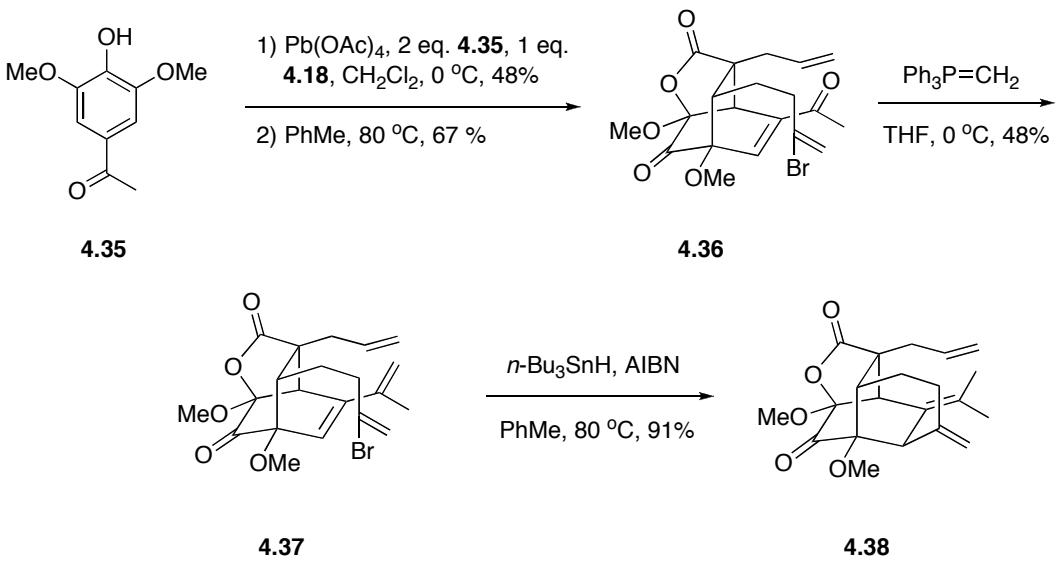
Given this difficulty in utilizing double radical cyclizations to provide the two six-membered rings, we have begun a stepwise route that involves sequential rather than simultaneous cyclizations. Synthesis of the needed acid chain is shown in Scheme 4.5. Similar Horner-Wadsworth-Emmons homologation of the same aldehyde **4.26** with known phosphonate **4.31**[20] provides ester **4.32**. Removal of the silyl protecting group is readily accomplished with tetrabutylammonium fluoride, after

which *B*-Br-9-BBN,[21] hydrodemetallation with acetic acid, and ester hydrolysis give the vinyl bromide **4.33**. Similarly, **4.32** can be taken to the vinyl iodide **4.34** using the same steps but substituting *B*-I-9-BBN.



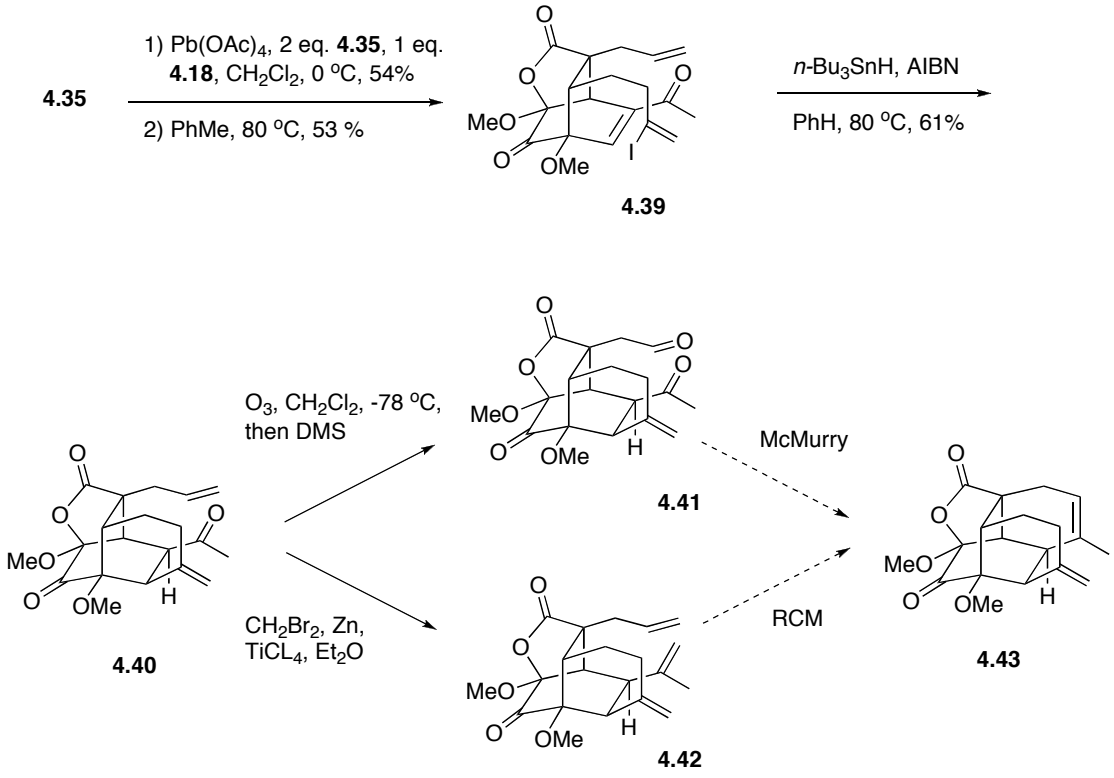
Scheme 4.5. Construction of the sidechains for stepwise cyclization route.

Oxidative dearomatization (Scheme 4.6) in this case utilizes the commercially available 3',5'-dimethoxy-4'-hydroxyacetophenone (**4.35**). This is noteworthy, as a full *eight* of vinigrol's 20 carbons and one of the necessary oxygens are provided in a single purchased compound. Subsequent Diels-Alder cycloaddition gives the necessary bicycle **4.36,** whose structure was verified by X-ray crystallography. Selective Wittig olefination of the acyclic ketone proved facile, giving **4.37** in anticipation of a future ring-closing olefin metathesis reaction. Unfortunately, radical cyclization, while competent in forming the desired front ring, occurs with migration to the tertiary alkene (**3.38**). It is noteworthy, though, that no 5-*exo*-trig cyclization was seen, further indicating the difficulty in a tandem cyclization process.



4.35 **4.36** **4.37** **4.38**

Scheme 4.6. Monocyclization with alkene migration.



4.39 **4.40** **4.41** **4.42** **4.43**

Scheme 4.7. Monocyclization; steps towards second cyclization.

Leaving functional group modification until after cyclization, we chose to generate bicycle **4.39** as radical initiation proved much milder with the vinyl iodide (Scheme 4.7). Treatment with *n*-Bu_3SnH and AIBN then provides the monocyclized adduct **4.40**, and we were quite pleased to find that the acetyl stereocenter is properly set by the bulky stannane approaching away from the allyl chain. Treatment of **4.40** with ozone can be used to access the aldehyde **4.41**, setting the stage for a McMurry[22] or pinacol[23] coupling. Otherwise, olefination to **4.42** using the Takai-Lombardo[24] reagent provides a substrate for ring-closing olefin metathesis. Attempts with both of these routes to form **4.43** are ongoing.

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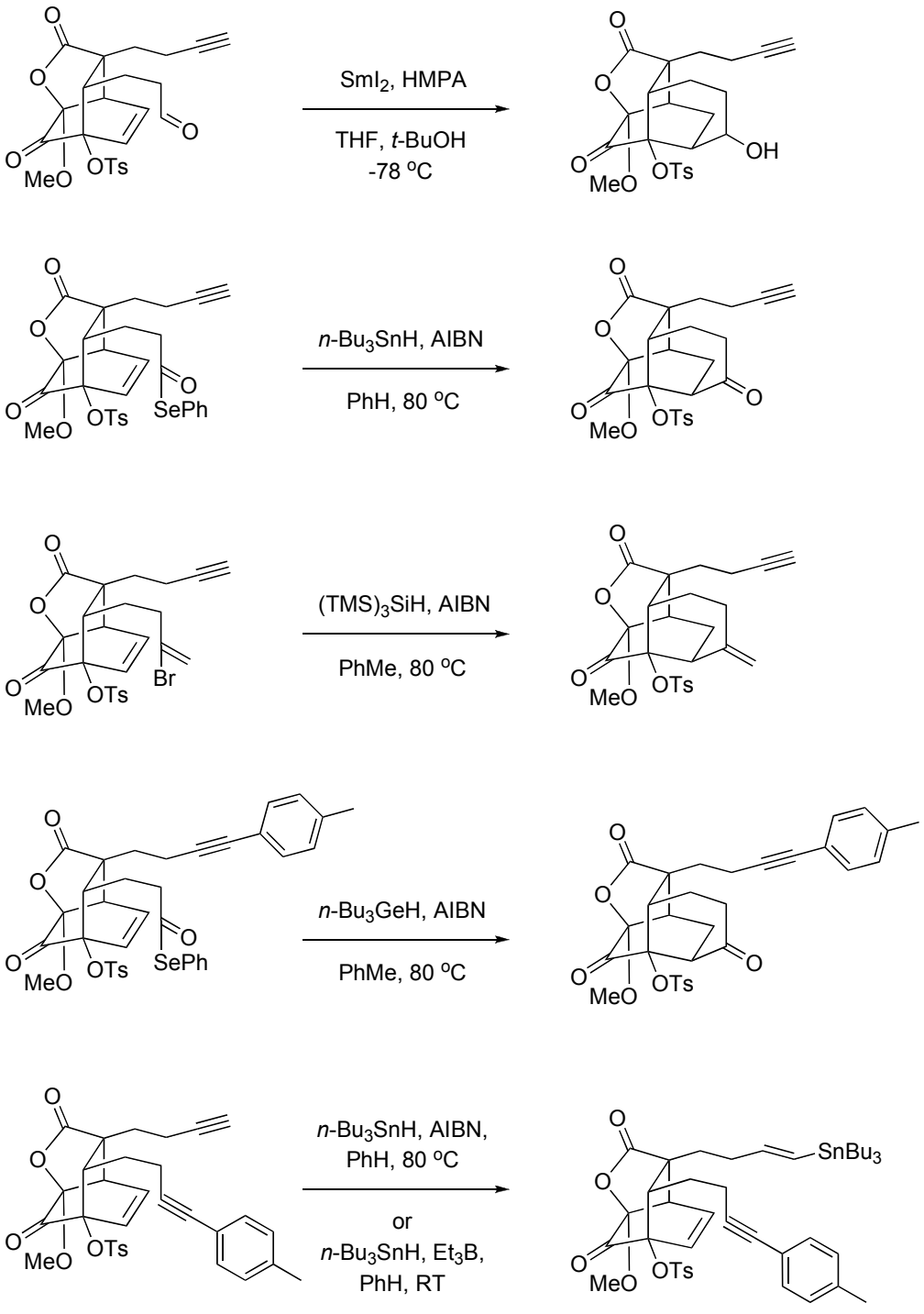
APPENDIX 1

The following tandem radical cyclizations were also attempted, with preliminary spectroscopic evidence suggesting the results shown.

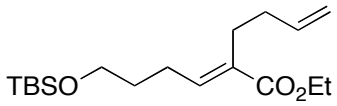


Scheme A1.1. Other failed tandem radical cyclizations.

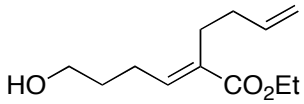
APPENDIX 2

A2.1 Experimental Procedures for Chapter 2

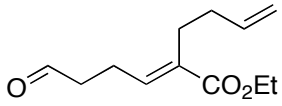
General Information: Commercial reagents were purchased and used without further purification. Toluene, dichloromethane, benzene, and THF were dried over a column of alumina prior to use. 1,1,1,3,3,3-Hexafluoro-2-propanol was redistilled from CaH_2 and stored over 4Å molecular sieves. Flash chromatography was performed with MP Silitech 32-63D 60Å silica, while thin layer chromatography (TLC) was performed with EMD 250 μm silica gel 60-F_{254} plates. NMRs were acquired on Varian Mercury 300 or Inova 500 or 600 MHz spectrometers and referenced to residual protic solvent. IR spectroscopic information was collected on a Nicolet Avatar 370 OTGS spectrometer. High-resolution mass spectrometry was obtained at the University of Illinois at Urbana-Champaign facility.



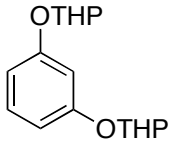
(*E*)-Ethyl 2-(but-3-enyl)-6-(*tert*-butyldimethylsilyloxy)hex-2-enoate (2.9): To a flame-dried flask under N_2 atmosphere was added the phosphonate **2.7** (2.23 g, 8.00 mmol, 1.2 eq.) dissolved in 25 ml of anhydrous toluene. The solution was brought to 0 ºC and *t*-BuOK (898 mg, 8.00 mmol, 1.2 eq.) was added. After stirring for 25 min., the pale yellow solution was brought to –78 ºC and aldehyde **2.8** (1.35 g, 6.67 mmol, 1.0 eq.) dissolved in 25 ml anhydrous toluene was added slowly via cannula. The solution was kept at –78 ºC for 1.5 hr, after which time the cooling bath was removed and the reaction mixture allowed to warm slowly to room temperature. The reaction was then quenched with sat. NH_4Cl and separated with Et_2O (3x). The combined organic layers were dried with Na_2SO_4, concentrated, and a crude NMR was obtained indicating a 9:1 ratio between the *E*:*Z* isomers. Flash chromatography (SiO_2; 2.5 → 5% Et_2O/pentane) gave the pure E olefin **2.9** (684 mg) as a colorless oil, with the remainder as a mixture of *E* and *Z* isomers (1.78 g total product obtained, 82% overall yield). ^{1}H-NMR (300 MHz, C_6D_6) δ 6.94 (t, *J*=7.60 Hz, 1H), 5.84 (ddt, J_1=6.73 Hz, J_2=10.12 Hz, J_3=16.92 Hz), 5.13-4.93 (m, 2H), 4.05 (q, *J*=7.11 Hz, 2H), 3.41 (t, *J*=6.01 Hz, 2 H), 2.60-2.46 (m, 2H), 2.28 (dd, J_1=7.01 Hz, J_2=14.92 Hz, 2H), 2.13 (dd, J_1=7.53 Hz, J_2=14.98 Hz, 2H), 1.53-1.34 (m, 2H), 1.01 (t, *J*=7.11 Hz, 3H), 0.95 (s, 9H), 0.01 (s, 6H); ^{13}C-NMR (75 MHz, C_6D_6) δ 167.2, 142.3, 138.3, 132.5, 115.1, 62.3, 60.2, 33.9, 32.2, 26.8, 26.1, 25.3, 18.4, 14.3, -5.3; FTIR (thin film/KCl) 2955, 2929, 2857, 1712, 1645, 1556, 1259, 1194, 1102, 911, 836, 776 cm^{-1}; HRMS (EI) *m*/*z* found 326.2282 [calc'd for $C_{18}H_{34}O_3Si$: 326.2277].



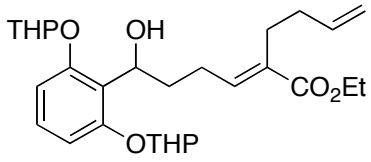
(*E*)-Ethyl 2-(but-3-enyl)-6-hydroxyhex-2-enoate (2.10a): Enoate **2.9** (3.74 g, 11.6 mmol) was dissolved in 108 ml wet THF and brought to 0 ºC, after which 12 ml 1M HCl was added. The cooling bath was removed after 5 min and consumption of starting material was monitored by TLC. Upon consumption of starting material, brine was added and the free alcohol extracted with EtOAc (3x). The combined organic layers were then dried with Na_2SO_4 and concentrated to give a colorless oil which was used in the next step without further purification. ^{1}H-NMR (500 MHz, C_6D_6) δ 6.89 (t, *J*=7.59 Hz, 1H), 5.80 (ddt, J_1=6.75 Hz, J_2=10.16 Hz, J_3=16.98 Hz, 1H), 5.07-4.91 (m, 2H), 4.02 (q, *J*=7.11 Hz, 2H), 3.43 (t, *J*=6.33 Hz, 2H), 2.75 (s, 1H) 54-2.38 (m, 2H), 2.23 (dd, J_1=6.99 Hz, J_2=15.04 Hz, 2H), 2.12 (dd, J_1=7.55 Hz, J_2=15.04 Hz, 2H), 1.54-1.41 (m, 2H), 1.00 (t, *J*=7.11 Hz, 3H); ^{13}C-NMR (126 MHz, C_6D_6) δ 167.6, 142.6, 138.3, 132.5, 115.1, 61.7, 60.4, 33.8, 32.1, 26.6, 25.2, 14.3; FTIR (thin film/KCl) 3340, 3078, 2979, 2939, 2871, 1708, 1642, 1445, 1368, 1262, 1199, 1134, 1053, 912, 751 cm^{-1}; HRMS (EI) *m/z* found 212.1407 [calc'd for $C_{12}H_{20}O_3$: 212.1413].



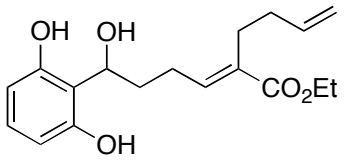
(*E*)-Ethyl 2-(but-3-enyl)-6-oxohex-2-enoate (2.10): To a flame-dried flask under N_2 was added $(COCl)_2$ (1.34 ml, 14.1 mmol, 1.5 eq.) dissolved in 15 ml anhydrous CH_2Cl_2 and the mixture was cooled to –78 ºC. Dimethylsulfoxide (2.3 ml, 28.3 mmol, 3.0 eq.) dissolved in 10 ml of dry CH_2Cl_2 was added slowly via addition funnel with venting of the effervescence. The reaction was allowed to stir 10 min, then alcohol **2.10a** (2 g, 9.42 mmol, 1.0 eq.) dissolved in 10 ml anhydrous CH_2Cl_2 was added via addition funnel. After 15 min, Et_3N (6.6 ml, 47 mmol, 5 eq.) was added and the reaction mixture brought to ambient temperature. Filtration through Celite, concentration, and flash chromatography (20% EtOAc/hexanes) gave the aldehyde **2.10** (1.69 g, 85% yield, 2 steps) as a yellow oil. ^{1}H-NMR (300 MHz, C_6D_6) δ 9.18 (t, *J*=0.90 Hz, 1H), 6.66 (t, *J*=7.50 Hz, 1H), 5.75 (ddt, J_1=6.74 Hz, J_2=10.13 Hz, J_3=16.92 Hz, 1H), 5.07-4.83 (m, 2H), 4.01 (q, *J*=7.11 Hz, 2H), 2.39 (t, *J*=7.55 Hz, 2H), 2.19 (dd, J_1=7.20 Hz, J_2=14.21 Hz), 2.08 (q, *J*=7.33 Hz, 2H), 1.82 (t, *J*=7.33 Hz, 2H), 0.99 (t, *J*=7.11 Hz, 3H); ^{13}C-NMR (75 MHz, C_6D_6) δ 199.3, 167.0, 140.4, 138.2, 133.0, 115.2, 60.3, 42.5, 33.6, 26.6, 21.1, 14.3; FTIR (thin film/KCl) 3081, 2978, 2935, 2827, 2727, 1709, 1643, 1447, 1367, 1268, 1196, 1136, 1054, 913, 751 cm^{-1}; HRMS (EI) *m/z* found 210.1264 [calc'd for $C_{12}H_{18}O_3$: 210.1256].



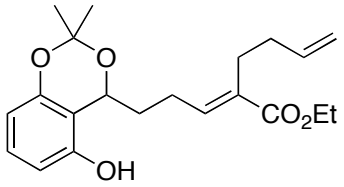
1,3-Bis(tetrahydro-2*H*-pyran-2-yloxy)benzene (2.11): To a flame-dried flask under N_2 atmosphere were combined resorcinol (2g, 18.2 mmol, 1 eq.), 3,4-dihydro-2*H*-pyran (3.95 ml, 43.6 mmol, 2.4 eq.), and pyridinium *p*-toluenesulfonate (46 mg, 0.182 mmol, 0.01 eq.) in 25 ml anhydrous CH_2Cl_2. The reaction was stirred at ambient temperature overnight, then water and saturated sodium bicarbonate were added and the organic layer separated with CH_2Cl_2 (x3). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 20% Et_2O/pentane) gave the desired **2.11** (4.83 g, 95% yield) as a white solid. ^{1}H-NMR (400 MHz, C_6D_6) δ 7.27 (t, *J*=2.16 Hz, 1H), 7.12 (d, *J*=8.39 Hz, 1H), 6.98-6.89 (m, 2H), 5.36 (t, *J*=2.96 Hz, 1H), 5.32 (t, *J*=2.98 Hz, 1H), 3.87-3.71 (m, 2 H), 3.40-3.31 (m, 2H), 1.91-.172 (m, 2H), 1.71-1.58 (m, 2H), 1.58-1.44 (m, 2H), 1.42-1.21 (m, 4H), 1.21-1.08 (m, 2H); ^{13}C-NMR (75 MHz, C_6D_6) δ 159.06, 158.98, 130.00, 129.00, 110.05, 109.99, 110.05, 109.99, 105.91, 105.52, 96.42, 96.20, 61.44, 61.38, 30.56, 30.53, 25.46, 18.80, 18.72; FTIR (thin film, KCl) 2943, 2874, 2851, 1602, 1488, 1356, 1259, 1203, 1152, 1038, 1000, 901, 872, 767, 688 cm^{-1}; HRMS (ES) *m/z* found 301.1416 (M+Na) [calc'd for $C_{16}H_{22}O_4Na$: 301.1416].



(*E*)-Ethyl 6-(2,6-bis(tetrahydro-2*H*-pyran-2-yloxy)phenyl)-2-(but-3-enyl)-6-hydroxy-hex-2-enoate (2.12): To a flame-dried flask under N_2 atmosphere were combined **2.11a** (239 mg, 0.859 mmol, 1.0 eq.) and TMEDA (0.15 ml, 1.02 mmol, 1.2 eq.) in 4.3 ml anhydrous Et_2O. This reaction mixture was brought to –78 ºC, then *t*-BuLi (0.54 ml, 0.86 mmol, 1.0 eq.) was added dropwise and the solution became yellow. After 20 min, aldehyde **2.10** (181 mg, 0.859 mmo, 1.0 eq.) dissolved in 4.3 ml anhydrous Et_2O was added dropwise. Stirring was continued at –78 ºC for 1.5 h, after which the solution was brought to 0 ºC for 15 min before quenching with water. The organic layer was extracted with EtOAc (x3), dried with Na_2SO_4, and concentrated. Column chromatography (SiO_2; 40 → 50% Et_2O/pentane) gave **2.12** (282 mg, 67% yield) as a slightly yellow oil containing an inseparable mixture of diastereomers which was carried to the next step without full characterization.

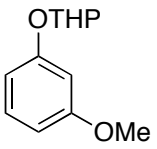


(*E*)-Ethyl 2-(but-3-enyl)-6-(2,6-dihydroxyphenyl)-6-hydroxyhex-2-enoate (2.13a): Benzylic alcohol **2.12** (210 mg, 0.430 mmol, 1.0 eq.) was dissolved in 3.6 ml THF and 0.9 ml H_2O, then brought to 0 ºC. To this solution was added 0.23 ml 1M HCl, then after 0.5 h another 0.23 ml portion of 1M HCl was added and the reaction mixture brought to 35ºC. Consumption of starting material was monitored by TLC (6 h), then brine added and the organic layer was separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4, concentrated, and subjected to column chromatography (SiO_2; 20 → 30 → 40% EtOAc/hexanes) to give the acid-sensitive triol **2.13a** (107 mg, 78% yield) as a colorless oil. ^{1}H-NMR (500 MHz, C_6D_6) δ 6.90 (t, *J*=7.52 Hz, 1H), 6.87 (t, *J*=8.07 Hz, 1H), 6.27 (d, *J*=8.11 Hz, 2H), 5.79 (ddt, J_1=6.82 Hz, J_2=10.11 Hz, J_3=16.96 Hz, 1H), 5.08-5.04 (m, 1H), 5.10-4.90 (m, 2H), 4.02 (q, *J*=7.10 Hz), 2.49-2.38 (m, 2H), 2.22 (dd, J_1=7.14 Hz, J_2=14.94 Hz, 2H), 2.18-2.09 (m, 2H), 1.91-1.77 (m, 2H), 1.77-1.62 (m, 2H), 0.98 (t, *J*=7.12 Hz, 3H); ^{13}C-NMR (125 MHz, C_6D_6) δ 168.2, 155.9, 143.1, 138.2, 132.2, 129.0, 115.2, 114.8, 108.4, 69.9, 60.6, 35.5, 33.8, 26.6, 25.0, 14.2; FTIR (thin film, KCl) 3383, 2980, 2932, 2869, 1684, 1646, 1559, 1472, 1291, 1272, 1208, 998, 913, 785, 668, 604 cm^{-1}; HRMS (EI) *m/z* found 320.1624 [calc'd for $C_{18}H_{24}O_5$: 320.1624].

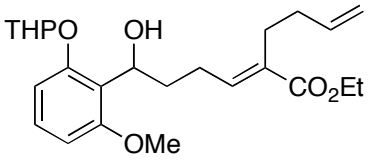


(*E*)-Ethyl 2-(3-(5-hydroxy-2,2-dimethyl-4*H*-benzo[*d*][1,3]dioxin-4-yl)ropylidene)-ex-5-enoate (2.13): To a flame-dried flask under N_2 atmosphere was added triol **2.13a** (4.7 mg, 14.7 μmol, 1.0 eq.) dissolved in 0.2 ml anhydrous CH_2Cl_2. Crushed molecular sieves (4Å; 4.7 mg), 2-methoxy-1-propene (1.7 μl, 17.6 μmol, 1.2 eq.), and PPTS (0.4 mg, 1.5 μmol, 0.1 eq.) were sequentially added and the reaction mixture stirred at ambient temperature for 8h. Saturated $NaHCO_3$ was added, then brine, and the organic layers separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4, concentrated, and subjected to column chromatography (SiO_2; 30 → 40% EtOAc/hexanes) to provide the acetonide **2.13** (3.3 mg, 62% yield). ^{1}H-NMR (500 MHz, C_6D_6) δ 7.10 (t, *J*=7.38 Hz, 1H), 6.89 (t, *J*=8.23 Hz, 1H), 6.62 (dd, J_1=0.92 Hz, J_2=8.17 Hz, 1H), 6.16 (d, *J*=8.01 Hz, 1H), 5.88 (s, 1H), 5.81 (ddt, J_1= 6.76 Hz, J_2=10.15 Hz, J_3=16.96 Hz, 1H), 5.20-4.88 (m, 2H), 3.99 (q, *J*=7.11, 2H), 2.52-2.38 (m, 2H), 2.54-2.46 (m, 2H), 2.38-2.27 (m, 2H), 2.24 (dd, J_1=7.09 Hz, J_2=15.10 Hz, 2H), 1.56 (s, 3H), 1.25 (s, 3H). 0.95 (t, *J*=7.12 Hz, 3H); ^{13}C-NMR (125 MHz, C_6D_6) δ

168.4, 154.1, 153.2, 144.2, 138.4, 131.9, 128.5, 115.1, 111.1, 110.0, 107.8, 99.2, 68.3, 60.6, 33.9, 32.4, 28.5, 26.5, 24.4, 21.4, 14.2; FTIR (thin film, KCl) 3381, 3076, 2989, 2938, 2852, 1683, 1638, 1618, 1594, 1467, 1374, 1270, 1206, 1150, 1033, 911, 887, 785, 741, 668 cm^{-1}; HRMS (ES) *m/z* found 383.1827 (M+Na) [calc'd for $C_{21}H_{28}O_5Na$: 383.1834].

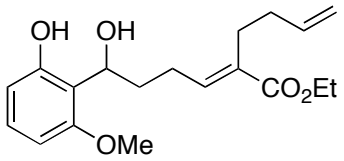


2-(3-Methoxyphenoxy)tetrahydro-2*H*-pyran (2.16): To a flame-dried flask under N_2 atmosphere was combined 3-methoxyphenol (10 g, 81.0 mmol, 1 eq.), 3,4-dihdro-2*H*-pyran (17.7 ml, 19.3 mmol, 2.4 eq.), and pyridinium *p*-toluenesulfonate (20 mg, 0.08 mmol, 0.01 eq.) in 80 ml anhydrous CH_2Cl_2. The reaction was allowed to stir at ambient temperature overnight, then water and saturated $NaHCO_3$ were added. The organic layers were separated with CH_2Cl_2 (x3), dried with Na_2SO_4, and concentrated *in vacuo*. Column chromatography (10% EtOAc/hexanes) gave the desired **2.16** (16.2 g, 96%) as a colorless, viscous oil. ^{1}H-NMR (400 MHz, C_6D_6) δ 7.10 (t, *J*=8.18 Hz, 1H), 6.94 (t, *J*=2.31 Hz, 1H), 6.89 (ddd, J_1=0.86 Hz, J_2=2.27 Hz, J_3=8.19 Hz, 1H), 6.54 (ddd, J_1=0.85 Hz, J_2=2.42 Hz, J_3=8.22 Hz, 1H), 5.31 (t, *J*=2.95 Hz, 1Hz), 3.78 (td, J_1=2.90 Hz, J_2=10.98 Hz, 1H), 3.44-3.34 (m, 1H), 3.33 (s, 3H), 1.91-1.77 (m, 1H), 1.73-1.62(m, 1H), 1.59-1.46 (m, 1H), 1.43-1.21 (m, 2H), 1.21-1.08 (m, 1H); ^{13}C-NMR (75 MHz, C_6D_6) δ 161.4, 159.1, 130.1, 109.1, 107.4, 103.3, 96.3, 61.4, 54.7, 30.5, 25.4, 18.8; FTIR (thin film, KCl) 2944, 2875, 2851, 1602, 1491, 1455, 1388, 1356, 1284, 1198, 1152, 1109, 1039, 973, 902, 872, 845, 766, 688 cm^{-1}; HRMS (EI) *m/z* found 208.1098 [calc'd for $C_{12}H_{16}O_3$: 208.1100]

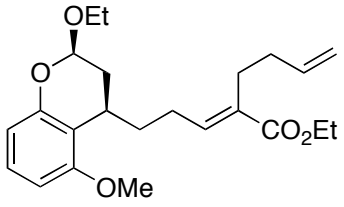


(*E*)-Ethyl 2-(but-3-enyl)-6-hydroxy-6-(2-methoxy-6-(tetrahydro-2*H*-pyran-2-yl-oxy)phenyl)-hex-2-enoate (2.17): To a flame-dried flask under N_2 atmosphere was added **2.16** (651 mg, 2.34 mmol, 1.5 eq.) and TMEDA (0.51 ml, 3.43 mmol, 2.2 eq.) in 11.7 ml anhydrous Et_2O. The reaction mixture was brought to –78 ºC, then *t*-BuLi (1.31 ml of a 1.32 M solution in pentane, 1.72 mmol, 1.1 eq.) was added dropwise. After 2 h, the lightly yellow solution was brought to –40 ºC. After an additional 2 h, a canula was used to transfer this solution into a solution at -78ºC containing the aldehyde **2.10** (329 mg, 1.56 mmol, 1.0 eq.) in 7.8 ml anhydrous Et_2O. This mixture

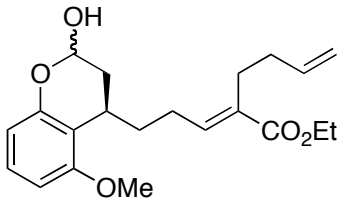
was stirred for 1 h, after which the cooling bath was removed and the reaction allowed to warm to ambient temperature. Saturated NH_4Cl and was then added and the organic layer extracted with EtOAc (x3), dried with Na_2SO_4, and concentrated *in vacuo*. Column chromatography (SiO_2; 10 → 20 → 30% EtOAc/hexanes) gave recovered **2.16** (232 mg) and **2.17** (678 mg, 83% yield) of the desired product as a 1:1 mixture of diastereomers. ^{1}H-NMR (500 MHz, C_6D_6) δ 7.08 (t, *J*=7.61 Hz, 2H), 7.03-6.90 (m, 4H), 6.28-6.22 (m, 2H), 5.89-5.75 (m, 1H), 5.62-5.48 (m, 1H), 5.28 (t, *J*=2.71 Hz, 1H), 5.19 (t, *J*=3.00 Hz, 1H), 5.07-4.90 (m, 4H), 4.11-3.99 (m, 4H), 3.97 (d, *J*=11.68 Hz, 1H), 3.89 (d, *J*=11.61 Hz, 1H), 3.74-3.59 (m, 2H), 3.38-3.27 (m, 2H), 3.21 (s, 6H), 2.65-2.50 (m, 4H), 2.50-2.36 (m, 6H), 2.36-2.25 (m, 4H), 2.25-2.13 (m, 2H), 2.02-1.89 (m, 2H), 1.82-1.63 (m, 4H), 1.63-1.38 (m, 4H), 1.22-1.03 (m, 2H), 1.03-0.92 (m, 6H); ^{13}C-NMR (125 MHz, C_6D_6) δ 167.34, 167.33, 158.16, 158.12, 155.77, 155.27, 142.88, 142.87, 138.45, 138.44, 132.43, 132.39, 128.43, 128.35, 121.35, 121.13, 114.96 (2C), 108.70, 108.34, 105.07, 104.92, 97.11, 96.00, 67.67, 67.63, 61.79, 61.46, 60.12 (2C), 55.12 (2C), 37.51, 37.48, 33.95, 33.93, 30.47, 30.43, 26.80, 26.77, 26.04, 25.95, 25.29, 25.24, 19.03, 18.74, 14.33 (2C); FTIR (thin film, KCl) 3553, 3075, 2943, 2832, 1706, 1642, 1596, 1472, 1442, 1357, 1266, 1202, 1120, 1081, 1038, 980, 902, 782, 734 cm^{-1}; HRMS (EI) *m/z* found 418.2354 [calc'd for $C_{24}H_{34}O_6$: 418.2355]



(*E*)-Ethyl 2-(but-3-enyl)-6-hydroxy-6-(2-hydroxy-6-methoxyphenyl)hex-2-enoate (2.18): Benzylic alcohol **2.17** (250 mg, 0.597 mmol) was dissolved in 4.8 ml THF and 1.2 ml H_2O at ambient temperature. To this was added 0.6 ml of 1M H_2SO_4 and the reaction monitored by TLC for completion (~4h). Brine was then added and the organic layer separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 20% EtOAc/hexanes) gave the diol product **2.18** (178 mg, 89% yield) as a colorless, slightly acid-sensitive oil that was immediately used in the next step. ^{1}H-NMR (500 MHz, C_6D_6) δ 9.06 (s, 1H), 6.98 (t, *J*=8.21 Hz, 1H), 6.89 (t, *J*=7.49 Hz, 1H), 6.77 (d, *J*=8.23 Hz, 1H), 6.11 (d, *J*=8.22 Hz, 1H), 5.77 (ddt, J_1=6.76 Hz, J_2=10.01 Hz, J_3=16.89 Hz, 1H), 5.22 (dt, J_1=4.39 Hz, J_2=8.52 Hz, 1H), 5.06-4.90 (m, 2H), 3.99 (t, *J*=7.11 Hz, 2H), 3.30 (s, 3H), 2.86 (d, *J*=3.98 Hz, 1H), 2.43 (t, *J*=7.60 Hz, 1H), 2.27-2.13 (m, 4H), 1.90 (dq, J_1=7.42 Hz, J_2=7.30 Hz, J_3=7.82 Hz, 1H), 1.80-1.67 (m, 1H), 0.98 (t, *J*=7.10 Hz, 3H); ^{13}C-NMR (125 MHz, C_6D_6) δ 167.7, 158.2, 156.7, 142.7, 138.3, 132.3, 129.0, 115.9, 115.1, 110.9, 101.9, 69.8, 60.4, 55.0, 35.7, 33.8, 26.7, 25.1, 14.2; FTIR (thin film, KCl) 3412, 3310, 2978, 2940, 2841, 1707, 1640, 1616, 1593, 1471, 1374, 1271, 1232, 1048, 914, 782, 730, 632 cm^{-1}; HRMS (EI) *m/z* found 334.1780 [calc'd for $C_{19}H_{26}O_5$: 334.1780].

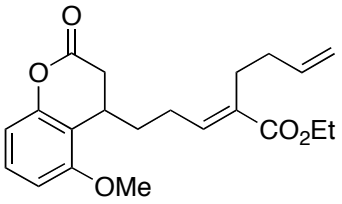


(*E*)-Ethyl 2-(3-(2-ethoxy-5-methoxychroman-4-yl)propylidene)hex-5-enoate (2.19): To a flame-dried flask under N_2 was added the diol **2.18** (200 mg, 0.598 mmol, 1.0 eq.), 12 ml ethyl vinyl ether, and 1.5 ml anhydrous CH_2Cl_2. The solution was brought to –78 ºC and trichloroacetylisocyanate (75 µl, 0.628 mmol, 1.05 eq.) in 2.5 ml anhydrous CH_2Cl_2 was added dropwise. After 10 min, the reaction mixture was brought to 0 ºC and allowed to stir at this temperature for 20 min before *in vacuo* removal of the solvent. Column chromatography (10% EtOAc/hexanes) gave the acetal **2.19** (188 mg, 81% yield) and 13.5 mg of styrene byproduct. ^{1}H-NMR (500 MHz, C_6D_6) δ 7.17 (t, *J*=7.10 Hz, 1H), 7.02 (t, *J*=8.19 Hz, 1H), 6.79 (d, *J*=8.16 Hz, 1H), 5.87 (ddt, J_1=6.78 Hz, J_2=10.16 Hz, J_3=16.93 Hz, 1H), 5.12-4.95 (m, 2H), 5.00 (dd, J_1=2.39 Hz, J_2=3.24 Hz, 1H), 4.05 (q, *J*=7.12 Hz, 2H), 3.80 (dqd, J_1=0.72 Hz, J_2=7.05 Hz, J_3=7.04 Hz, J_4=9.59 Hz, 1H), 3.37 (s, 3H), 3.32 (dqd, J_1=0.72 Hz, J_2=0.74 Hz, J_3=7.02 Hz, J_4=9.61 Hz, 1H), 3.03-2.97 (m, 1H), 2.64-2.54 (m, 2H), 2.37-2.23 (m, 4H), 2.23-2.07 (m, 2H), 1.96 (dt, J_1=1.72 Hz, J_2=14.18 Hz, 1H), 1.64 (ddd, J_1=3.27 Hz, J_2=6.98 Hz, J_3=14.16 Hz, 1H), 0.99 (t, *J*=7.10 Hz, 3H); ^{13}C-NMR (125 MHz, C_6D_6) δ 167.3, 158.1, 152.8, 143.3, 138.5, 132.1, 127.6, 115.7, 115.0, 110.5, 103.0, 97.5, 64.1, 60.1, 55.0, 34.0, 33.0, 28.6, 27.9, 27.0, 26.8, 15.4, 14.3; FTIR (thin film, KCl) 3075, 2976, 2933, 2839, 1708, 1642, 1592, 1468, 1375, 1264, 1180, 1129, 1086, 911, 777, 727, 605 cm^{-1}; HRMS (EI) *m/z* found 388.2250 [calc'd for $C_{23}H_{32}O_5$: 388.2250].

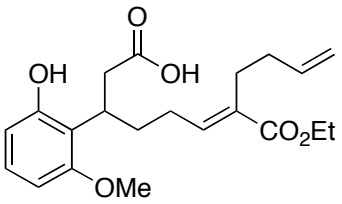


(*E*)-Ethyl 2-(3-(2-hydroxy-5-methoxychroman-4-yl)propylidene)hex-5-enoate (2.20a): To a solution of acetal **2.19** (102 mg, 0.263 mmol, 1.0 eq.) in 1.3 ml MeCN and 1.3 ml H_2O was added camphorsulfonic acid (304 mg, 1.31 mmol, 5.0 eq.) and the reaction mixture heated to 40 ºC. After 8 h, the reaction was diluted with brine and

the organic layer separated with EtOAc (x3). The organic layers were combined, dried with Na_2SO_4, and concentrated *in vacuo*. Column chromatography (SiO_2; 20 → 30% EtOAc) gave the product **2.20a** (58.1 mg, 87% yield) along with 12.9 mg recovered **2.19** with acetal stereochemistry scrambled (99% BRSM). Product **2.20a** was then used in the next step without full characterization.

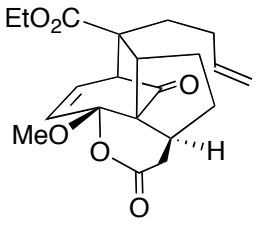


(*E*)-Ethyl 2-(3-(5-methoxy-2-oxochroman-4-yl)propylidene)hex-5-enoate (2.20): Hemiacetal **2.20a** was dissolved in 3.8 ml acetone at 0 °C. To this solution was slowly added 0.35 ml of Jones' reagent (prepared from 25g CrO_3, 25 ml H_2SO_4, and 75 ml H_2O). The reaction went from red to green as the oxidant was consumed, until towards end of addition the reaction mixture remained red. The solution was allowed to stir for 15 min, after which excess oxidant was consumed through addition of 0.35 ml 2-propanol. The mixture was diluted with H_2O and the organic layer separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 20% EtOAc) yielded the lactone **2.20** (121 mg, 89% yield) as a viscous, colorless oil. ^{1}H-NMR (500 MHz, C_6D_6) δ 6.86 (t, *J*=8.30 Hz, 1H), 6.75 (t, *J*=7.35 Hz, 1H), 6.65 (d, *J*=8.18 Hz, 1H), 6.18 (d, *J*=8.29 Hz, 1H), 5.75 (ddt, J_1=6.73 Hz, J_2=10.20 Hz, J_3=17.04 Hz, 1H), 5.08-4.91 (m, 2H), 4.05 (q, *J*=7.07 Hz, 2H), 2.99 (ddd, J_1=2.86 Hz, J_2=7.27 Hz, J_3=13.75 Hz, 1H), 2.45-2.30 (m, 3H), 2.19 (dd, J_1=6.94 Hz, J_2=15.85 Hz, 1H), 1.93-1.77 (m, 2H), 1.42-1.31 (m, 1H), 1.29-1.18 (m, 1H); ^{13}C-NMR (125 MHz, C_6D_6) δ 167.2, 166.8, 156.8, 152.9, 141.7, 138.2, 132.4, 128.7, 115.4, 115.2, 110.0, 106.1, 60.2, 55.1, 33.80, 33.75, 33.3, 29.2, 26.8, 25.9, 14.3; FTIR (thin film, KCl) 3076, 2977, 2037, 2851, 1773, 1705, 1644, 1594, 1467, 1363, 1267, 1150, 1089, 912, 785, 739, 668 cm^{-1}; HRMS (EI) *m/z* found 358.1786 [calc'd for $C_{21}H_{26}O_5$: 358.1780].

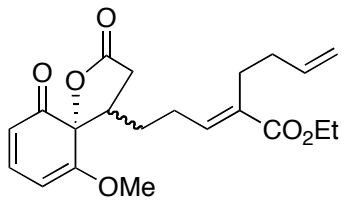


(*E*)-7-(Ethoxycarbonyl)-3-(2-hydroxy-6-methoxyphenyl)undeca-6,10-dienoic acid (2.21): Lactone **2.20** (45 mg, 126 μmol, 1.0 eq.) was dissolved in 0.65 ml THF at 0 °C and 0.65 ml of 1M NaOH then added. Monitoring by TLC indicated complete

consumption of starting material within 2.5 h. The reaction mixture was then brought to pH ~1 through addition of 1.3 ml 1M HCl and the organic layer separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4, concentrated *in vacuo*, and used in the oxidative dearomatization step without further purification.



2.22 and **2.23**

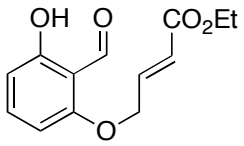


Oxidative dearomatization to [5+2] adduct 2.22 and spiroquinols 2.23: Crude acid **2.21** (105 mg, 0.293 mmol, 1.0 eq.) was dissolved in 5 ml 1,1,1,3,3,3-hexafluoro-2-propanol and brought to 0 ºC. Iodobenzene diacetate (104 mg, 0.322 mmol, 1.1 eq.) was added. The reaction mixture immediately turned yellow, then green. After 15 minutes, TLC showed consumption of all starting material. The solvent was removed *in vacuo* and the residue chromatographed (SiO_2; 20 → 30→ 40% EtOAc/hexanes) to provide the spiroquinols **2.23** (34.0 mg, 2.5:1 mixture of diastereomers; brilliant yellow in solution, tacky orange oil when neat) and the [5+2] adduct **2.22** (37.2 mg) as a colorless oil (65% overall yield).

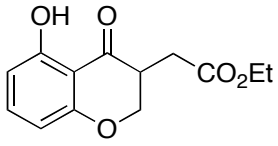
2.22: ^{1}H-NMR (400 MHz, C_6D_6) δ 5.88 (dd, J_1=7.12 Hz, J_2=9.75 Hz, 1H), 5.66 (d, J=9.75 Hz, 1H), 5.56, (ddt, J_1=6.51 Hz, J_2=10.17 Hz, J_3=16.81 Hz, 1H), 5.03-4.81 (m, 2H), 3.90-3.67 (m, 2H), 3.50 (dd, J_1=7.24 Hz, J_2=11.84 Hz, 1H), 2.91 (d, J=7.12 Hz, 1H), 2.87 (s, 3H), 2.64 (dd, J_1=7.90 Hz, J_2=15.10 Hz, 1H), 2.49 (tt, J_1=7.06 Hz, J_2=11.30 Hz, 1H), 2.21 (dd, J_1=10.04 Hz, J_2=15.12 Hz, 1H), 1.96-1.76 (m, 2H), 1.76-1.60 (m, 2H), 1.51 (dddd, J_1=5.66 Hz J_2=10.82 Hz, J_3=13.87 Hz, J_4=17.12 Hz, 2H), 1.31-1.18 (m, 1H), 1.07 (ddd, J_1=5.93 Hz, J_2=12.28 Hz, J_3=25.39 Hz, 1H), 0.82 (t, J=7.11 Hz, 3H); ^{13}C-NMR (75 MHz, C_6D_6) δ 204.5, 173.2, 169.1, 137.2, 132.7, 123.1, 115.4, 109.7, 65.2, 60.8, 56.4, 53.5, 49.4, 47.0, 38.2, 35.2, 34.8, 32.0, 30.3, 27.7, 14.1; gCOSY, HSQC, and gHMBC also available; FTIR (thin film, KCl) 3075, 2976, 2949, 2870, 1767, 1729, 1640, 1451, 1382, 1284, 1186, 1124, 971, 865, 788, 751, 545 cm^{-1}; HRMS (EI) *m/z* found 374.1730 [calc'd for $C_{21}H_{26}O_6$: 374.1729].

2.23: ^{1}H-NMR (400 MHz, C_6D_6) δ **Major isomer:** 6.66 (t, J=7.44 Hz, 1H), 6.22 (dd, J_1=7.14 Hz, J_2=9.81 Hz, 1H), 5.79-5.67 (m, 1H), 5.67 (dd, J_1=0.62 Hz, J_2=9.81 Hz, 1H), 5.06-4.90 (m, 2H), 4.38 (d, J=7.11 Hz, 1H), 4.02 (q, J=7.11 Hz, 2H), 2.70 (s, 3H), 2.64-2.42 (m, 1H), 2.42-2.27 (m, 2H), 2.27-2.03 (m, 3H), 1.70-1.51 (m, 2H), 1.41-1.26 (m, 1H), 1.21-1.04 (m, 1H), 1.02-0.86 (m, 1H), 0.969 (t, J=7.11 Hz, 3H); **Minor isomer**: 6.63 (t, J=7.38 Hz, 1H), 6.20 (dd, J_1=7.17 Hz, J_2=9.79 Hz, 1H), 5.79-5.67 (m, 1H), 5.55 (dd, J_1=0.62 Hz, J_2=9.80 Hz, 1H), 5.06-4.90 (m, 2H), 4.46 (d, J=7.09 Hz, 1H), 4.03 (q, J=7.11 Hz, 2H), 2.94 (s, 3H), 2.64-2.42 (m, 1H), 2.42-2.27

(m, 2H), 2.27-2.03 (m, 3H), 1.70-1.51 (m, 2H), 1.21-1.04 (m, 2H), 1.02-0.86 (m, 1H), 0.969 (t, *J*=7.11 Hz, 3H); ^{13}C-NMR (125 MHz, C_6D_6) δ **Major isomer**: 195.72, 174.56, 167.00, 164.68, 143.15, 140.68, 138.01, 132.86, 118.49, 115.34, 95.58, 85.61, 60.45, 55.18, 47.59, 34.22, 33.74, 28.70, 27.23, 26.66, 14.27; **Minor isomer**: 197.11, 174.38, 166.96, 164.06, 143.86, 140.54, 138.01, 133.04, 118.55, 115.32, 95.48, 85.56, 60.42, 55.63, 45.85, 33.68, 31.98, 30.17, 28.70, 26.98, 14.27; **Both:** FTIR (thin film, KCl) 2977, 2917, 2849, 1792, 1703, 163, 1631, 1550, 1450, 1366, 1266, 1237, 1186, 1141, 1068, 1017, 918, 801, 627 cm^{-1}; HRMS (EI) *m/z* found 374.1729 [calc'd for $C_{21}H_{26}O_6$: 374.1729].

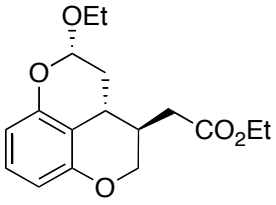


(*E*)-Ethyl 4-(2-formyl-3-hydroxyphenoxy)but-2-enoate (2.26): To a flame-dried flask under N_2 atmosphere was added 2,5-dihydroxybenzaldehyde (2.0 g, 14.5 mmol, 1.0 eq.) dissolved in 30 ml anhydrous DMF. Crotyl bromide (2.15 ml, 15.9 mmol, 1.1 eq.) was added followed by K_2CO_3 (2.4 g, 17.4 mmol, 1.2 eq.). The solution was stirred for 4 h, then filtered through Celite with EtOAc to remove remaining solid K_2CO_3. The organic layer was washed with 2 portions water, 1 portion brine, dried with Na_2SO_4 and concentrated. Column chromatography (SiO_2; 20 → 30% EtOAc/hexanes) provided the mono-crotylated product (2.57 g, 71% yield) as a yellow oil. ^{1}H-NMR (500 MHz, C_6D_6) δ 12.47 (s, 1H), 10.15 (s, 1H), 6.92-6.72 (m, 2 H), 6.48 (d, *J*=8.42 Hz), 6.00 (d, *J*=15.80 Hz, 1H), 5.59 (d, *J*=8.24 H, 1H), 4.04 (t, *J*=7.09 Hz), 3.87-3.73 (m, 2H), 1.00 (t, *J*=7.10 Hz); ^{13}C-NMR (125 MHz, C_6D_6) δ 193.7, 165.4, 164.3, 160.7, 141.2, 138.0, 122.4, 111.2, 110.7, 101.7, 66.6, 60.6, 14.2; FTIR (thin film, KCl) 2980, 2901, 2771, 1719, 1645, 1577, 1459, 1385, 1308, 1241, 1180, 1108, 1040, 967, 837, 784, 718, 604 cm^{-1}; HRMS (EI) *m/z* found 250.0841 [calc'd for $C_{13}H_{14}O_5$: 250.0841].



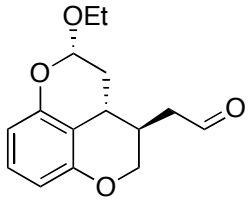
Ethyl 2-(5-hydroxy-4-oxochroman-3-yl)ethanoate (2.27): To a flame-dried flask under N_2 atmosphere was added **2.26** (2.5g, 10.0 mmol, 1.0 eq.) dissolved in 20 ml

anhydrous CH_2Cl_2. 3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride (270 mg, 01.0 mmol, 0.1 eq.) and *i*-Pr_2NEt (0.87 ml, 5.0 mmol, 0.5 eq.) were added and the resultant orange/red solution stirred at ambient temperature for 4 h. Saturated NH_4Cl was added and the organic layer separated with CH_2Cl_2 (x3). The combined organic layers were dried with Na_2CO_4, concentrated, and subjected to column chromatography (SiO_2; 20% EtOAc/hexanes) to give the chromanone **2.27** (2.16 g, 86% yield) as a yellow crystalline solid. ^{1}H-NMR (500 MHz, C_6D_6) δ 6.88 (t, *J*=8.29 Hz, 1H), 6.50 (dd, J_1=0.82 Hz, J_2=8.32 Hz, 1H), 6.28 (dd, J_1=0.83 Hz, J_2=8.22 Hz, 1H), 3.94-3.82 (m, 4H), 3.63 (t, *J*=11.49 Hz, 1H), 2.90-2.82 (m, 1H), 2.44 (dd, J_1=4.76 Hz, J_2=17.08 Hz, 1H), 1.90 (dd, J_1=7.80 Hz, J_2=17.08 Hz, 1H), 0.90 (td, J_1=0.56 Hz, J_2=7.13 Hz, 3H); ^{13}C-NMR (125 MHz, C_6D_6) δ 198.9, 170.6, 163.0, 162.1, 138.3, 109.6, 108.1, 107.2, 69.5, 60.7, 41.8, 29.8, 14.1; FTIR (thin film, KCl) 3446, 3057, 2936, 2904, 1734, 1644, 1580, 1463, 1364, 1224, 1179, 1115, 1065, 1104, 948, 921, 803, 730 cm^{-1}; HRMS (EI) *m/z* found 250.0841 [calc'd for $C_{13}H_{14}O_5$: 250.0841.

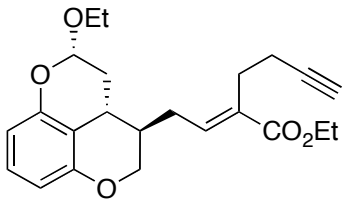


Acetal 2.28: A flask was charged with **2.27** (199 mg, 0.795 mmol, 1.0 eq.) dissolved in 2.5 ml MeOH and brought to 0 ºC. $NaBH_4$ (60 mg, 1.6 mmol, 2.0 eq.) was carefully added with much evolution of gas. The reaction was allowed to stir for 20 min, then quenched with 1M HCl to pH ~1. Brine was added and the organic layer separated with EtOAc (x3), dried with Na_2SO_4, and concentrated. Flash chromatography (SiO_2; 50% EtOAc/hexanes) afforded an acid-sensitive diol which was immediately dissolved in 8.0 ml ethyl vinyl ether in a flame-dried flask under N_2 atmosphere. The solution was brought to –78 ºC and trichloroacetylisocyanate (3.5 ml, 0.88 mmol, 1.1 eq.) added. After 5 min the reaction mixture was removed from the cooling bath and allowed to warm to ambient temperature. The reaction mixture was concentrated *in vacuo* and subjected to flash chromatography (SiO_2; 10 → 20% EtOAc/hexanes) to give the benzopyran **2.28** (208 mg, 85% yield) as a white solid. ^{1}H-NMR (300 MHz, C_6D_6) δ 6.95 (t, *J*=8.13 Hz, 1H), 6.68-6.59 (m, 2H), 4.93 (dd, J_1=3.05 Hz, J_2=9.51 Hz, 1H), 4.21 (dd, J_1=3.54 Hz, J_2=10.71 Hz, 1H), 4.02 (dq, J_1=7.08 Hz, J_2=9.37 Hz, 1H), 3.84 (q, *J*=7.13 Hz, 2H), 3.54 (t, *J*=10.84 Hz, 1H), 3.42 (dq, J_1=7.07 Hz, J_2=9.45 Hz, 1H), 2.27-2.11 (m, 1H), 2.05-1.76 (m, 3H), 1.63 (dd, J_1=7.81 Hz, J_2=15.35 Hz, 1H), 1.36 (td, J_1=9.56 Hz, J_2=12.68 Hz, 1H), 1.15 (t, *J*=7.07 Hz, 3H), 0.89 (t, *J*=7.13 Hz, 3H); ^{13}C-NMR (75 MHz, C_6D_6) δ 170.9, 154.3, 154.2, 129.0, 108.8, 108.6, 108.3, 100.3, 69.6, 64.1, 60.4, 34.2, 33.7, 33.2, 32.2, 15.4, 14.1; FTIR (thin film, KCl) 2977, 2932, 2876, 1733, 1612, 1589, 1472, 1377, 1327, 1266, 1242, 1147, 1069, 1024, 917, 880, 780, 726 cm^{-1}; HRMS (EI) *m/z* found 306.1468

[calc'd for $C_{17}H_{22}O_5$: 306.1467].

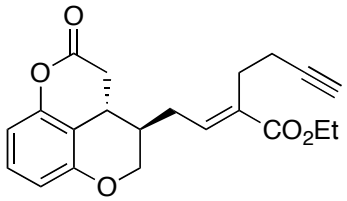


Aldehyde 2.30a: In a flame-dried flask under N_2 atmosphere was dissolved **2.28** (1.14 g, 43.72 mmol, 1.0 eq.) in 30 ml anhydrous toluene and the solution brought to –78 ºC. DIBAL-H (3.27 ml of a 20 wt% soln., 4.60 mmol, 1.2 eq.) was added dropwise down the inner wall of the flask in order to bring it to –78 ºC as it entered the reaction mixture. After allowing the reaction mixture to stir for 15 min., an aqueous solution of 20 wt% Rochelle's salt was added and the reaction mixture removed from the cooling bath and allowed to stir until a clean separation of the organic and aqueous layers was obtained. Separation with EtOAc (x3), drying of the combined organic layers with Na_2SO_4, and concentration *in vacuo* gave the aldehyde as a crude, semi-solid white material used in the next step without further purification. ^{1}H-NMR (500 MHz, C_6D_6) δ 8.98 (t, *J*=1.60 Hz, 1H), 6.96 (td, J_1=0.64 Hz, J_2=12.63 Hz, 1H), 6.64 (dd, J_1=3.09 Hz, J_2=12.63 Hz, 1H), 6.62 (dd, J_1=0.93 Hz, J_2=12.67 Hz, 1H), 4.89 (dd, J_1=3.09 Hz, J_2=9.50 Hz, 1H), 4.04 (dq, J_1=7.08 Hz, J_2=9.41 Hz, 1H), 3.92 (dd, J_1=3.61 Hz, J_2=10.72 Hz, 1H), 3.44 (dq, J_1=7.07 Hz, J_2=9.38 Hz, 1H), 3.30 (t, *J*=10.88 Hz, 1H), 1.99 (ddd, J_1=4.24 Hz, J_2=10.87 Hz, J_3=12.74 Hz, 1H), 1.72 (ddd, J_1=3.17 Hz, J_2=4.21 Hz, J_3=12.64 Hz, 1H), 1.69-1.62 (m, 1H), 1.59 (ddd, J_1=1.32 Hz, J_2=4.56 Hz, J_3=17.20 Hz, 1H), 1.32-1.19 (m, 1H), 1.17 (t, *J*=7.07 Hz, 3H); ^{13}C-NMR (125 MHz, C_6D_6) δ 198.5, 154.3, 154.1, 129.1, 108.64, 108.55, 108.4, 100.2, 69.2, 64.2, 43.3, 33.1, 32.3, 31.3, 15.4; FTIR (thin film, KCl) 2969, 2925, 2875, 2734, 1844, 1723, 1588, 1472, 1325, 1264, 1146, 1074, 1022, 917, 874, 781, 727 cm^{-1}; HRMS (EI) *m/z* found 262.1206 [calc'd for $C_{15}H_{18}O_4$: 262.1205].



Alkyne 2.30: To a flame-dried flask under N_2 atmosphere was dissolved phosphonate **2.29** (1.24 g, 4.48 mmol, 1.2 eq.) in 22 ml dry toluene. The solution was brought to 0 ºC and *t*-BuOK (502 mg, 4.48 mmol, 1.2 eq.) added. The reaction mixture was allowed to stir at 0 ºC for 20 min, brought to ambient temperature for 10 min, and then

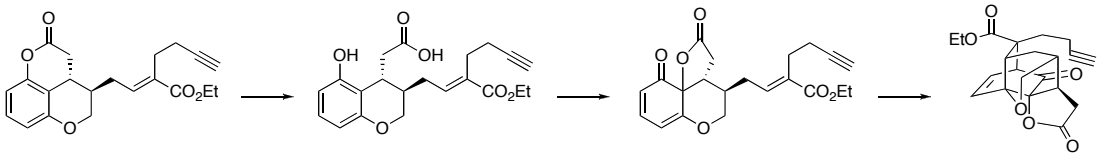
cooled to –78 ºC. A solution of the crude aldehyde **2.30a** in 19 ml anhydrous toluene was added dropwise and the reaction mixture stirred for 1 h, after which the cooling bath was removed and the reaction mixture allowed to slowly warm to ambient temperature. Saturated NH_4Cl was added and the organic layer was separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4, concentrated *in vacuo*, and subjected to column chromatography (SiO_2; 10 → 20 → 30% EtOAc/hexanes) to give **2.30** (1.0 g, 70% yield) as a colorless oil. ^{1}H-NMR (500 MHz, C_6D_6) δ 6.98 (t, *J*=8.12 Hz, 1H), 6.72 (*J*=7.55 Hz, 1H), 6.66 (d, *J*=8.07 Hz, 1H), 6.62 (d, *J*=8.16 Hz, 1H), 4.98 (dd, J_1=2.96 Hz, J_2=9.47 Hz, 1H), 4.07 (dq, J_1=7.09 Hz, J_2=14.25 Hz, 1H), 4.03-3.92 (m, 3H), 3.47 (dq, J_1=7.00 Hz, J_2=14.07 Hz, 1H), 3.38 (t, *J*=11.08 Hz, 1H), 2.47-2.35 (m, 2H), 2.30 (dt, J_1=4.16 Hz, J_2=8.43 Hz, 1H), 2.18-2.08 (m, 1H), 2.03-1.91 (m, 2H), 1.71 (dd, J_1=1.98 Hz, J_2=2.63 Hz, 1H), 1.56 (dt, J_1=8.70 Hz, J_2=15.73 Hz, 1H), 1.33 (dt, J_1=9.74 Hz, J_2=12.75 Hz, 1H), 1.29-1.22 (m, 1H), 1.18 (t, *J*=7.35 Hz, 3H), 0.96 (td, J_1=0.54 Hz, J_2=7.09 Hz, 3H); ^{13}C-NMR (75 MHz, C_6D_6) δ 166.3, 154.3, 154.2, 140.35, 132.5, 128.9, 109.0, 108.5, 108.3, 100.3, 95.1, 83.6, 69.6, 64.3, 60.5, 36.3, 33.1, 32.3, 28.3, 26.2, 18.3, 15.5, 14.2; FTIR(thin film, KCl) 3284, 2976, 2933, 2883, 1709, 1612, 1583, 1470, 1380, 1325, 1264, 1195, 1147, 1065, 1026, 879, 780 cm^{-1}; HRMS (EI) *m/z* found 384.1937 [calc'd for $C_{23}H_{28}O_5$: 384.1937].



Lactone 2.31: To a solution of acetal **2.30** (950 mg, 2.47 mmol, 1.0 eq.) in 18 ml MeCN, 9 ml H_2O, and 4.5 ml THF was added camphorsulfonic acid (861 mg, 3.71 mmol, 1.5 eq.). The reaction mixture was heated at 50 ºC for 4.5 h, at which time TLC indicated consumption of starting material. Brine was added, and the organic layer separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The crude reaction product was then filtered through silica (30% EtOAc/hexanes) and reconcentrated *in vacuo*.

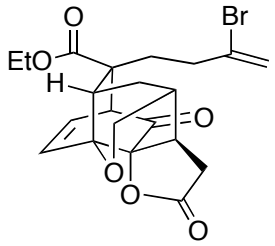
The above product hemiacetal was dissolved in 22.5 ml acetone at 0 ºC, after which 2.5 ml Jones' reagent (prepared from 25 g CrO_3, 25 ml H_2SO_4, and 75 ml H_2O) was added dropwise. The reaction went from red to green as the oxidant was consumed, until towards end of addition the reaction mixture remained red. The solution was allowed to stir for 10 min, after which excess oxidant was consumed through addition of 2.5 ml 2-propanol. The mixture was diluted with H_2O and brine and the organic layer was separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 10 → 20% EtOAc) yielded the lactone **2.31** (703 mg, 80% yield) as a viscous, colorless oil. ^{1}H-NMR (500 MHz, C_6D_6) δ 6.84 (t, *J*=8.17 Hz, 1H), 6.65-6.60 (m, 2H), 6.58 (d, *J*=8.02

Hz, 1H), 4.00 (qd, J_1=1.59 Hz, J_2=7.07 Hz, 2H), 3.85 (dd, J_1=3.51 Hz, J_2=11.10 Hz, 1H), 3.11 (t, J=11.20 Hz, 1H), 2.50 (dd, J_1=4.43 Hz, J_2=15.21 Hz, 1H), 2.44-2.32 (m, 2H), 2.33-2.24 (m, 2H), 1.92-1.83 (m, 1H), 1.76 (t, J=2.56 Hz, 1H), 1.70 (ddd, J_1=4.10 Hz, J_2=6.19 Hz, J_3=15.73 Hz, 1H), 1.42-1.27 (m, 2H), 1.13-1.01 (m, 1H), 0.98 (t, J=7.13, 3H); ^{13}C-NMR (125 MHz, C_6D_6) δ 166.4, 166.3, 154.0, 152.4, 139.7, 132.9, 129.2, 112.1, 109.1, 108.5, 83.4, 69.7, 69.0, 60.7, 36.4, 32.9, 31.7, 28.0, 26.2, 18.3, 14.2; FTIR (thin film, KCl) 3285, 2978, 2933, 2883, 1766, 1710, 1621, 1590, 1469, 1330, 1264, 1237, 1146, 1065, 1004, 784, 727 cm^{-1}; HRMS (EI) *m/z* found 354.1464 [calc'd for $C_{21}H_{22}O_5$: 354.1467].



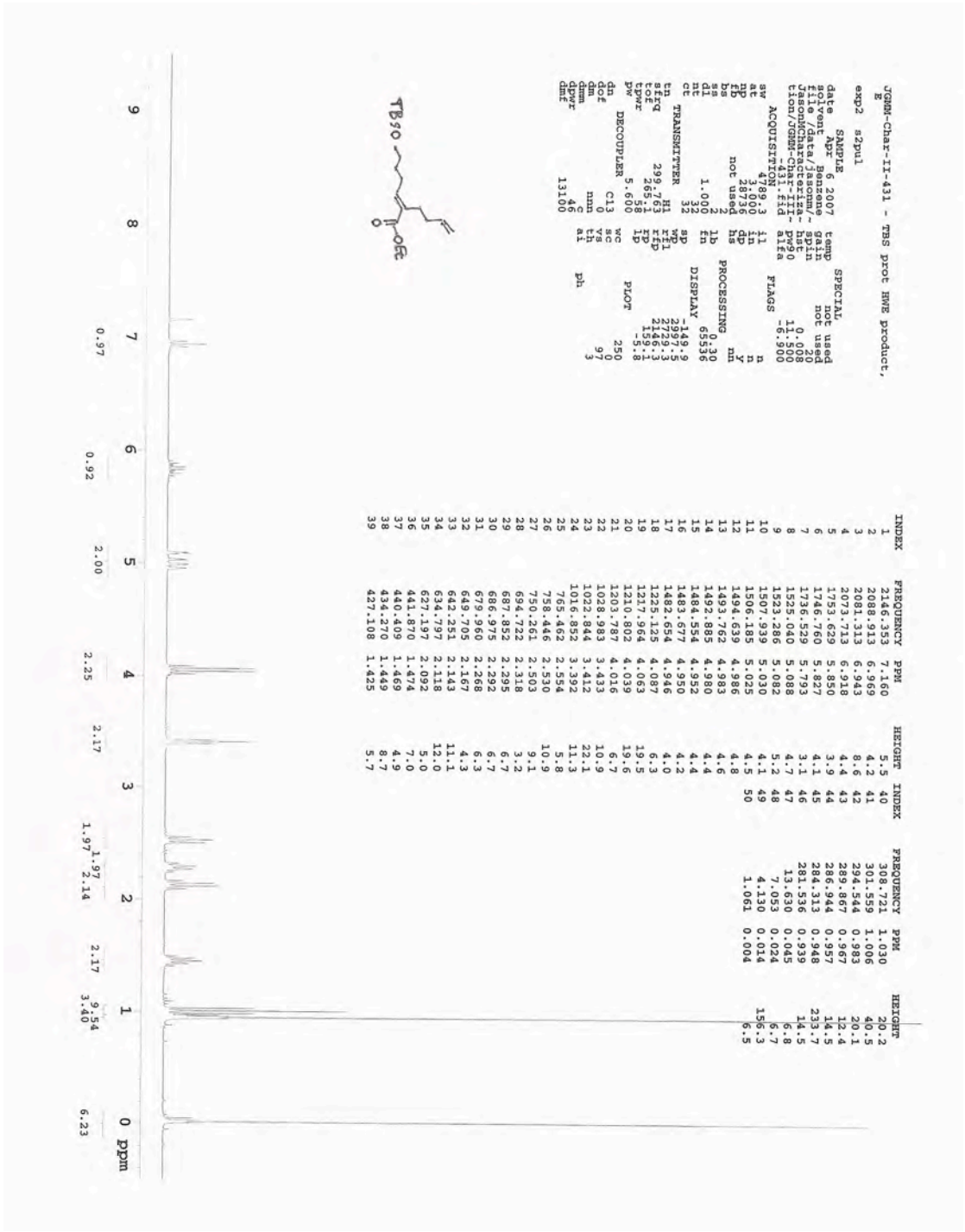
Bicycle 2.32: Lactone **2.31** (240 mg, 0.677 mmol, 1.0 eq.) was dissolved in 7 ml THF at 0 ºC and 3.5 ml of 1M NaOH was added. Consumption of starting material was monitored by TLC (1.5 h), after which 3.5 ml of 1M HCl was added to bring the reaction mixture to pH ~1. Brine was added and the organic layer separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo* to give the free acid/phenol which was immediately dissolved in 13.5 ml 1,1,1,3,3,3-hexafluoro-2-propanol (redistilled and stored over 4Å sieves) and brought to 0 ºC. Lead tetraacetate (330 mg, 0.745 mmol, 1.1 eq.) was added, the reaction mixture allowed to stir for 15 min, then 5 drops ethylene glycol were added to consume any excess oxidant. Solvent was removed *in vacuo* and the black residue immediately chromatographed (SiO_2; 30 → 40 → 50% EtOAc/hexanes) to provide the desired quinol contaminated with inseparable byproducts. This mixture was dissolved in 25 ml anhydrous toluene in a flame-dried flask under N_2 atmosphere and heated at 100 ºC. After 5 h, the solvent was removed *in vacuo* and the residue chromatographed (SiO_2; 30 → 40 → 50% EtOAc/hexanes) to provide the desired bicycle (21.2 mg, 8.4%) as a yellow semi-solid. ^{1}H-NMR (600 MHz, C_6D_6) δ 6.17 (dd, J_1=1.12 Hz, J_2=8.47 Hz, 1H), 5.56 (dd, J_1=6.35 Hz, J_2=8.44 Hz, 1H), 3.74 (dq, J_1=7.11 Hz, J_2=10.81 Hz, 1H), 3.63 (dq, J_1=7.12 Hz, J_2=10.81 Hz, 1H), 3.47 (dq, J_1=2.17 Hz, J_2=10.01 Hz, 1H), 3.32 (d, J=6.35 Hz, 1H), 3.25 (dd, J_1=3.34 Hz, J_2=9.99 Hz, 1H), 3.10 (dd, J_1=5.23 Hz, J_2=12.16 Hz, 1H), 2.33 (dd, J_1=11.48 Hz, J_2=18.75 Hz, 1H), 2.04 (dddd, J_1=2.58 Hz, J_2=5.90 Hz, J_3=11.13 Hz, J_4=16.93 Hz, 1H), 1.95-1.87 (m, 1H), 1.85-1.71 (m, 3H), 1.67-1.61 (m, 1H), 1.33 (ddd, J_1=3.16 Hz, J_2=12.29 Hz, J_3=13.98 Hz, 2H), 1.02 (ddt, J_1=2.80 Hz, J_2=5.40 Hz, J_3=13.98 Hz, 1H), 0.73 (t, J=7.10 Hz, 3H), 0.59-0.57 (m 1H); ^{13}C-NMR (determined by HSQC and gHMBC) δ 202.0, 171.8, 170.8, 135.0, 122.3, 80.2, 78.8, 71.5, 67.8, 61.2, 59.4, 54.3, 50.5, 36.6, 34.9, 32.7, 29.3, 28.8, 24.1, 13.2, 11.8; NOESY spectra were also obtained, verifying the structure; FTIR (thin film, KCl) 3278, 2978, 2917, 2849, 1791, 1703, 1673, 1633,

1550, 1455, 1368, 1237, 1187, 1016, 914, 802, 669 cm^{-1}; HRMS (EI) *m/z* found 370.1415 [calc'd for $C_{21}H_{22}O_6$: 370.1416].



Vinyl bromide 2.33: To a flame-dried flask under N_2 atmosphere was added bicycle **2.32** (5.7 mg, 0.0154 mmol, 1.0 eq.) dissolved in 0.3 ml anhydrous CH_2Cl_2. The reaction flask was cooled to 0 °C and a solution of 9-bromo-9-borabicyclo[3.3.1]nonane (30 µl of a 1.0 M sol. in CH_2Cl_2, 0.031 mmol, 2.0 eq.) was added. The reaction mixture was stirred for 4 h, then 0.03 ml AcOH was added and the reaction brought to ambient temperature. After 30 min, 0.06 ml 1M NaOH and 0.06 ml 30% H_2O_2 were added. The mixture was stirred vigorously for 1 h, then brine was added and the organic layer separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2, 30 → 40 → 50% EtOAc/hexanes) gave the product vinyl bromide **27** (6.0 mg, 86%) as a white solid. ^{1}H-NMR (600 MHz, C_6D_6) δ 6.21 (dd, J_1=1.22 Hz, J_2=8.50 Hz, 1H), 5.63 (dd, J_1=6.33 Hz, J_2=8.50 Hz, 1H), 5.24-5.20 (m, 2H), 3.79 (dq, J_1=7.10 Hz, J_2=10.75 Hz, 1H), 3.71 (dq, J_1=7.10 Hz, J_2=10.75 Hz, 1H), 3.49 (dt, J_1=2.28 Hz, J_2=10.00 Hz, 1H), 3.38 (dd, J_1=1.13 Hz, J_2=6.32 Hz, 1H), 3.28 (dt, J_1=1.82 Hz, J_2=10.00 Hz, 1H), 3.13 (dd, J_1=5.24 Hz, J_2=12.13 Hz, 1H), 2.34 (dd, J_1=12.15 Hz, J_2=19.43 Hz, 1H), 2.31-2.25 (m, 1H), 2.15-2.08 (m, 1H), 1.83 (dt, J_1=4.19 Hz, J_2=15.40 Hz, 2H), 1.75 (ddd, J1=5.41 Hz, J_2=11.77 Hz, J_3=13.78 Hz, 1h), 1.43-1.23 (m, 3H), 1.21-1.12 (m, 1H), 0.97-0.83 (m, 1H), 0.80 (t, J=7.12 Hz, 3H), 0.64-0.62 (m, 1H); FTIR (thin film, KCl) 2957, 2918, 2849, 1786, 1728, 1467, 1367, 1185, 1066, 892, 680 cm^{-1}; HRMS (EI) *m/z* found 450.0676 [calc'd for $C_{21}H_{23}O_6$: 450.0678].

A2.2 ^{1}H and ^{13}C NMR Spectra



13C OBSERVE

exp2 s2pul

SAMPLE		SPECIAL	
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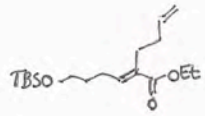
solvent	Benzene	gain	not used
file	/data/jasonm/~	spin	20
	JasonMCharacteriza-	hst	0.008
	tion/JGMM-Char-II--	pw90	17.100
	431c.fid	alfa	-8.800
ACQUISITION		**FLAGS**	
sw	18797.0	il	n
at	2.500	in	n
np	93984	dp	y
fb	not used	hs	nn
bs	4	**PROCESSING**	
d1	1.000	lb	1.00
nt	256	fn	131072
ct	100	**DISPLAY**	
TRANSMITTER		sp	-1082.2
tn	C13	wp	14707.5
sfrq	75.383	rfl	10746.0
tof	727.6	rfp	9648.0
tpwr	60	rp	134.7
pw	6.000	lp	18.0
DECOUPLER		**PLOT**	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	151
dmm	w	th	11
dpwr	40	ai	ph
dmf	11900		

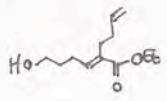
INDEX	FREQUENCY	PPM	HEIGHT
1	12602.237	167.194	14.3
2	10723.857	142.273	30.9
3	10426.999	138.335	28.3
4	9990.460	132.543	22.4
5	9672.091	128.320	166.0
6	9647.998	128.000	167.2
7	9623.905	127.680	165.1
8	8671.952	115.051	34.8
9	4694.915	62.287	35.6
10	4538.025	60.206	32.6
11	2557.537	33.931	37.1
12	2425.887	32.184	34.2
13	2018.317	26.777	30.8
14	1965.255	26.073	110.0
15	1905.310	25.278	36.8
16	1387.314	18.405	20.3
17	1079.844	14.326	29.4
18	-397.849	-5.278	55.7



JGMM-Char-1553 - TBS deprot, HWE product

expl s2pul

SAMPLE		DEC. & VT	
date	Apr 8 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
	JasonMCharacteriza~	dof	0
	tion/JGMM-Char-XI--	dm	nnn
	1553.fid	dmm	c
ACQUISITION		dmf	200
sfrq	499.920	dseq	
tn	H1	dres	1.0
at	1.892	homo	n
np	30272	temp	22.0
sw	8000.0	PROCESSING	
fb	4000	wtfile	
bs	4	proc	ft
tpwr	58	fn	not used
pw	5.5	math	f
d1	0		
tof	0	werr	
nt	320	wexp	wft
ct	28	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	99		
sc	35		
wc	215		
hzmm	23.22		
is	1167.59		
rfl	5072.3		
rfp	3579.4		
th	7		
ins	2.000		
nm	ph		



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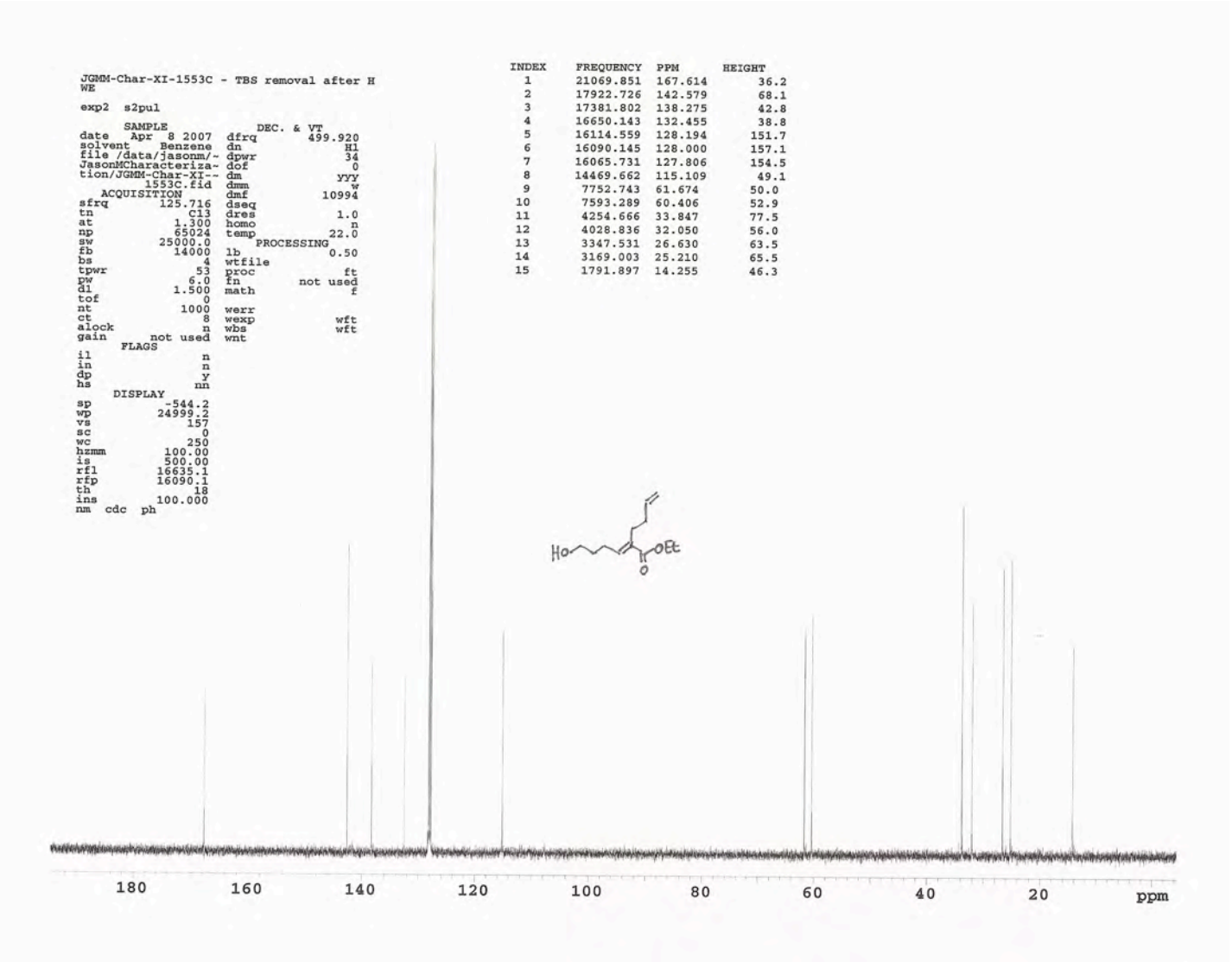
1	3451.478	6.904	11.4	40	738.099	1.476	21.9
2	3443.666	6.888	22.3	41	731.751	1.464	8.7
3	3436.341	6.874	11.4	42	507.630	1.015	62.1
4	2905.091	5.811	9.4	43	502.748	1.006	8.7
5	2898.255	5.797	9.6	44	500.306	1.001	99.3
6	2888.001	5.777	7.0	45	493.470	0.987	61.3
7	2524.232	5.049	11.7				
8	2522.279	5.045	12.9				
9	2507.142	5.015	10.9				
10	2505.189	5.011	11.7				
11	2478.822	4.958	11.4				
12	2477.845	4.957	11.0				
13	2476.869	4.955	11.0				
14	2468.568	4.938	11.3				
15	2467.591	4.936	10.5				
16	2466.615	4.934	10.5				
17	2022.767	4.046	16.3				
18	2015.443	4.032	57.6				
19	2008.119	4.017	53.4				
20	2001.283	4.003	19.3				
21	1719.544	3.440	22.8				
22	1713.197	3.427	45.3				
23	1706.849	3.414	23.5				
24	1377.259	2.755	11.0				
25	1241.029	2.482	23.5				
26	1233.705	2.468	36.4				
27	1225.404	2.451	29.9				
28	1124.330	2.249	10.6				
29	1117.982	2.236	21.8				
30	1116.517	2.233	22.0				
31	1109.681	2.220	21.7				
32	1102.357	2.205	8.2				
33	1069.154	2.139	15.4				
34	1061.830	2.124	38.0				
35	1054.505	2.109	38.0				
36	1046.693	2.094	17.1				
37	759.584	1.519	9.4				
38	753.236	1.507	22.8				
39	745.423	1.491	30.2				

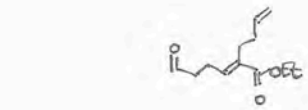

JGMM-Char-XI-1553C - TBS removal after H
WE
exp2 s2pul
SAMPLE
date Apr 8 2007
solvent Benzene
file /data/jasonm/~
JasonMCharacteriza~
tion/JGMM-Char-XI--
1553C.fid
ACQUISITION
sfrq 125.716
tn C13
at 1.300
np 65024
sw 25000.0
fb 14000
bs 4
tpwr 53
pw 6.0
dl 1.500
tof 0
nt 1000
ct 8
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -544.2
wp 24999.2
vs 157
sc 0
wc 250
hzmm 100.00
is 500.00
rfl 16635.1
rfp 16090.1
th 18
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.920
dn H1
dpwr 34
dof 0
dm yyy
dmm w
dmf 10994
dseq
dres 1.0
homo n
temp 22.0
PROCESSING
lb 0.50
wtfile
proc ft
fn not used
math f
werr
wexp wft
wbs wft
wnt
INDEX FREQUENCY PPM HEIGHT
1 21069.851 167.614 36.2
2 17922.726 142.579 68.1
3 17381.802 138.275 42.8
4 16650.143 132.455 38.8
5 16114.559 128.194 151.7
6 16090.145 128.000 157.1
7 16065.731 127.806 154.5
8 14469.662 115.109 49.1
9 7752.743 61.674 50.0
10 7593.289 60.406 52.9
11 4254.666 33.847 77.5
12 4028.836 32.050 56.0
13 3347.531 26.630 63.5
14 3169.003 25.210 65.5
15 1791.897 14.255 46.3
Ho
OEt
O
180
160
140
120
100
80
60
40
20
ppm

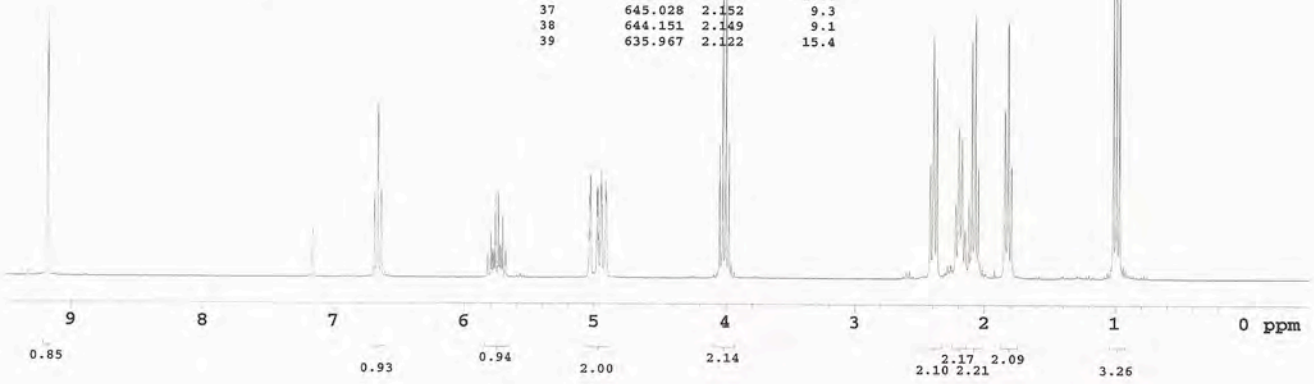
JGMM-Char-XI-1555 - Aldehyde side chain

exp1 s2pul

SAMPLE		SPECIAL	
date	Apr 11 2007	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/~	spin	20
JasonMCharacteriza~		hst	0.008
tion/JGMM-Char-XI-~		pw90	11.500
	1555.fid	alfa	-6.900
ACQUISITION		FLAGS	
sw	4789.3	il	n
at	3.000	in	n
np	28736	dp	y
fb	not used	hs	nn
bs	2	PROCESSING	
ss	2	lb	0.30
dl	1.000	fn	65536
nt	32	DISPLAY	
ct	4	sp	-149.9
TRANSMITTER		wp	2997.5
tn	H1	rf1	2729.0
sfrq	299.763	rfp	2146.3
tof	265.1	rp	158.0
tpwr	58	lp	-3.4
pw	5.600	PLOT	
DECOUPLER		wc	250
dn	C13	sc	0
dof	0	vs	171
dm	nnn	th	7
dmm	c	ai	ph
dpwr	46		
dmf	13100		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2752.904	9.184	42.4	40	628.659	2.097	45.2
2	2751.881	9.180	51.4	41	621.205	2.072	50.8
3	2751.004	9.177	24.1	42	613.897	2.048	21.5
4	2146.353	7.160	9.6	43	552.657	1.844	32.3
5	2004.142	6.686	16.6	44	545.349	1.819	48.9
6	1996.688	6.661	33.5	45	538.041	1.795	21.7
7	1989.234	6.636	17.0	46	303.606	1.013	75.3
8	1737.552	5.796	9.8	47	296.590	0.989	151.2
9	1727.321	5.762	15.8	48	289.428	0.966	74.8
10	1720.451	5.739	16.2				
11	1710.367	5.706	12.3				
12	1510.570	5.039	8.5				
13	1509.108	5.034	19.9				
14	1507.208	5.028	19.8				
15	1505.601	5.023	8.9				
16	1493.470	4.982	7.5				
17	1492.008	4.977	17.5				
18	1490.108	4.971	17.5				
19	1488.500	4.966	8.7				
20	1483.093	4.948	20.6				
21	1482.069	4.944	18.2				
22	1481.192	4.941	16.6				
23	1473.008	4.914	18.6				
24	1471.985	4.911	16.8				
25	1470.962	4.907	15.3				
26	1213.871	4.049	25.4				
27	1206.710	4.026	77.2				
28	1199.548	4.002	77.1				
29	1192.532	3.978	26.1				
30	725.122	2.419	22.0				
31	718.107	2.396	46.5				
32	710.068	2.369	38.4				
33	666.513	2.223	14.4				
34	659.644	2.201	28.4				
35	658.913	2.198	28.9				
36	651.898	2.175	27.0				
37	645.028	2.152	9.3				
38	644.151	2.149	9.1				
39	635.967	2.122	15.4				



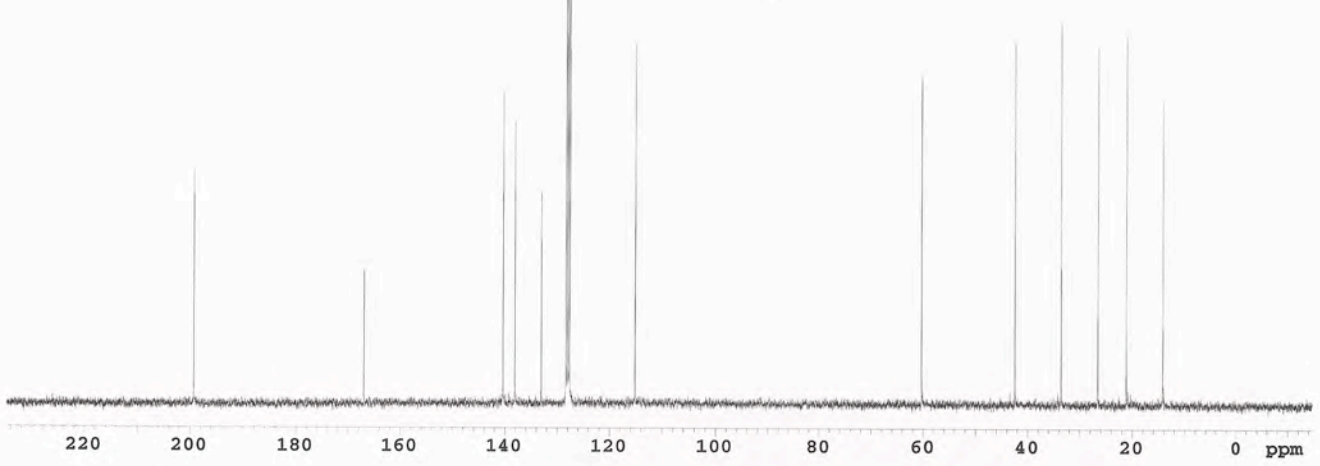


JGMM-Char-XI-1555 - Aldehyde side chain

exp2 s2pul

SAMPLE		SPECIAL	
date	Apr 11 2007	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/~	spin	20
JasonMCharacteriza~		hst	0.008
tion/JGMM-Char-XI--		pw90	17.100
	1555C.fid	alfa	-8.800
ACQUISITION		FLAGS	
sw	18797.0	il	n
at	2.500	in	n
np	93984	dp	y
fb	not used	hs	nn
bs	4	PROCESSING	
d1	1.000	lb	1.00
nt	320	fn	131072
ct	68	DISPLAY	
TRANSMITTER		sp	-1098.5
tn	C13	wp	18796.7
sfrq	75.383	rfl	10746.8
tof	727.6	rfp	9648.0
tpwr	60	rp	143.7
pw	6.000	lp	5.7
DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	128
dmm	w	th	12
dpwr	40	ai	ph
dmf	11900		

INDEX	FREQUENCY	PPM	HEIGHT
1	15019.838	199.268	44.3
2	12586.749	166.988	25.4
3	10582.742	140.401	59.0
4	10411.224	138.126	53.4
5	10026.026	133.015	40.2
6	9672.378	128.323	147.4
7	9647.998	128.000	148.9
8	9623.905	127.680	147.6
9	8682.277	115.188	68.4
10	4547.777	60.335	62.2
11	3203.454	42.500	68.6
12	2536.026	33.645	72.4
13	2005.123	26.602	68.0
14	1593.824	21.145	70.3
15	1074.394	14.254	57.6



JGMM-Char-III-436 - BisTHP resorcinol

expl s2pul

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solvent	Benzene	gain	not used
file	/data/jasonm/~	spin	not used
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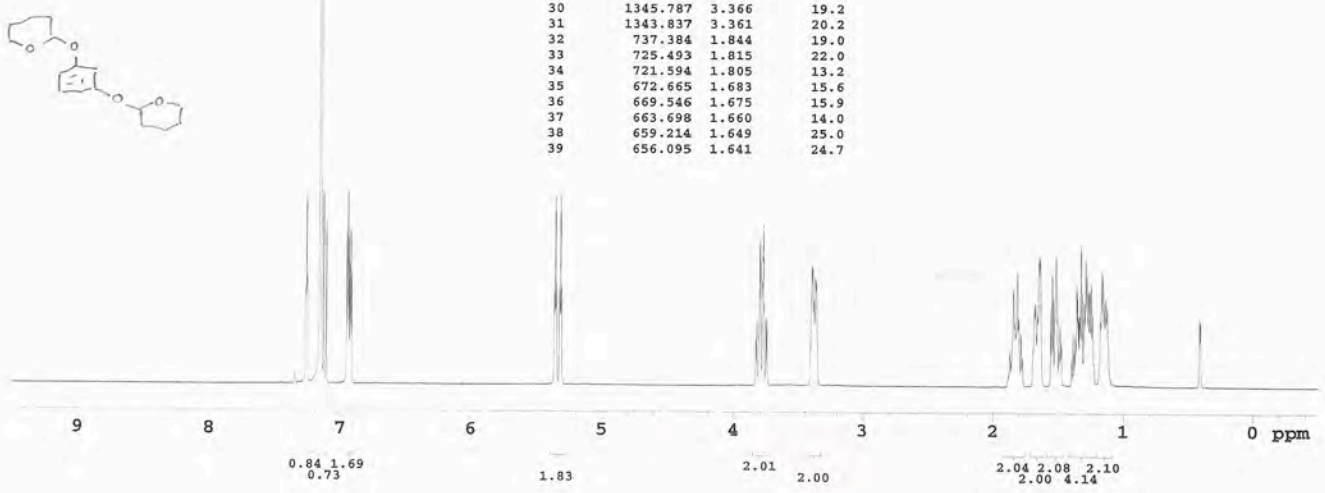
	tion/JGMM-Char-III~	pw90	12.900
	-436.fid	alfa	1.600
ACQUISITION		FLAGS	
sw	6387.7	il	n
at	3.744	in	n
np	47830	dp	y
fb	not used	hs	nn
bs	2	PROCESSING	
dl	1.000	fn	not used
nt	32	DISPLAY	
ct	14	sp	-200.1
TRANSMITTER		wp	3997.6
tn	H1	rfl	3627.6
sfrq	399.780	rfp	2862.4
tof	399.5	rp	-16.7
tpwr	53	lp	4.4
pw	6.450	is	265.152
DECOUPLER		PLOT	
dn		wc	250
dof	0	sc	0
dm	nnn	vs	140
dmm	c	th	13
dpwr	33	ai ph	
dmf	29412		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2907.242	7.272	19.2	40	622.371	1.557	14.9
2	2905.097	7.267	36.8	41	618.277	1.547	21.8
3	2902.758	7.261	21.3	42	614.768	1.538	17.1
4	2862.406	7.160	339.9	43	606.191	1.516	25.2
5	2852.074	7.134	36.6	44	601.512	1.505	13.2
6	2843.692	7.113	31.5	45	543.031	1.358	19.7
7	2780.922	6.956	29.5	46	540.887	1.353	17.1
8	2778.193	6.949	37.2	47	538.937	1.348	13.8
9	2775.269	6.942	29.6	48	536.598	1.342	13.4
10	2772.734	6.936	24.0	49	534.064	1.336	13.8
11	2769.810	6.928	29.7	50	529.970	1.326	27.0
12	2767.081	6.922	21.7	51	525.681	1.315	17.9
13	2145.423	5.367	18.2	52	519.833	1.300	16.3
14	2142.499	5.359	36.0	53	516.130	1.291	24.9
15	2139.575	5.352	19.3	54	512.231	1.281	21.4
16	2129.828	5.328	18.4	55	507.942	1.271	18.4
17	2126.904	5.320	36.4	56	503.653	1.260	18.3
18	2123.785	5.312	19.2	57	499.365	1.249	19.9
19	1521.231	3.805	28.0	58	494.881	1.238	14.0
20	1518.892	3.799	24.3	59	467.005	1.168	22.1
21	1512.849	3.784	20.2	60	463.106	1.158	21.8
22	1510.314	3.778	31.0	61	458.818	1.148	16.2
23	1507.975	3.772	16.3	62	454.334	1.136	16.9
24	1501.932	3.757	12.9	63	450.435	1.127	15.0
25	1499.008	3.750	13.2	64	166.995	0.418	13.2
26	1358.068	3.397	23.2				
27	1355.144	3.390	23.0				
28	1351.440	3.380	16.4				
29	1347.541	3.371	20.8				
30	1345.787	3.366	19.2				
31	1343.837	3.361	20.2				
32	737.384	1.844	19.0				
33	725.493	1.815	22.0				
34	721.594	1.805	13.2				
35	672.665	1.683	15.6				
36	669.546	1.675	15.9				
37	663.698	1.660	14.0				
38	659.214	1.649	25.0				
39	656.095	1.641	24.7				

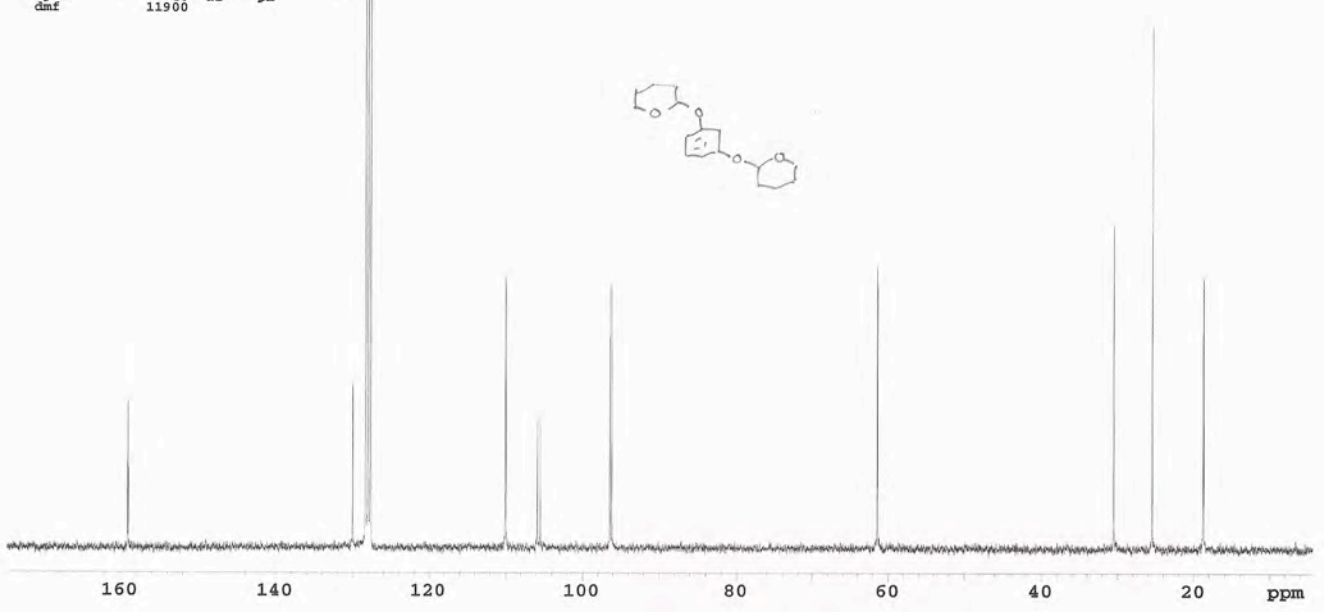


JGMM-Char-III-436C - bisTHP resorcinol

expl s2pul

SAMPLE		SPECIAL	
date	Apr 6 2007	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/~	spin	20
	JasonMCharacteriza-	hst	0.008
	tion/JGMM-Char-III-	pw90	17.100
	-436C.fid	alfa	-8.800
ACQUISITION		FLAGS	
sw	18797.0	il	n
at	2.500	in	n
np	93984	dp	y
fb	not used	hs	nn
bs	4	PROCESSING	
d1	1.000	lb	1.00
nt	256	fn	131072
ct	100	DISPLAY	
TRANSMITTER		sp	330.7
tn	C13	wp	12842.0
sfrq	75.383	rfl	10747.7
tof	727.6	rfp	9648.0
tpwr	60	rp	141.2
pw	6.000	lp	6.7
DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	160
dmm	w	th	10
dpwr	40	ai	ph
dmf	11900		

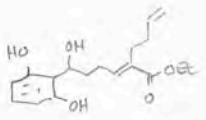
INDEX	FREQUENCY	PPM	HEIGHT
1	11989.305	159.062	27.7
2	11982.995	158.978	27.8
3	9798.865	130.002	31.3
4	9797.718	129.986	30.8
5	9672.091	128.320	176.0
6	9647.998	128.000	176.2
7	9623.619	127.677	174.5
8	8294.785	110.047	51.6
9	8290.482	109.990	49.9
10	7982.725	105.907	24.4
11	7953.470	105.519	24.9
12	7267.111	96.413	49.9
13	7250.475	96.192	50.2
14	4630.668	61.435	53.8
15	4625.792	61.370	52.7
16	2302.555	30.548	61.5
17	2300.547	30.521	60.2
18	1918.504	25.453	99.5
19	1415.996	18.786	51.4
20	1410.260	18.710	51.1



JGMM-Char-XI-1551 - Triol from first rou
te

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 6 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/--	dpwr	30
JasonMCharacteriza-		dof	0
tion/JGMM-Char-XI--		dm	nnn
	1551.fid	dmm	c
ACQUISITION		dmf	200
sfrq	499.920	dseq	
tn	H1	dres	1.0
at	1.892	homo	n
np	30272	temp	20.0
sw	8000.0	PROCESSING	
fb	4000	wtfile	
bs	4	proc	ft
tpwr	58	fn	not used
pw	5.5	math	f
dl	0		
tof	0	werr	
nt	320	wexp	wft
ct	48	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	132		
sc	35		
wc	215		
hzmm	23.22		
is	536.00		
rfl	5072.3		
rfp	3579.4		
th	6		
ins	2.000		
nm	ph		



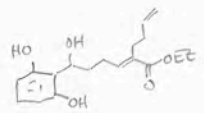
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3579.408	7.160	131.8	40	1057.923	2.116	8.9
2	3457.826	6.917	11.4	41	1055.970	2.112	9.9
3	3450.501	6.902	22.3	42	930.970	1.862	6.6
4	3444.642	6.890	18.1	43	924.623	1.850	9.6
5	3442.689	6.887	12.5	44	918.275	1.837	6.8
6	3436.830	6.875	31.9	45	916.810	1.834	12.3
7	3428.529	6.858	17.2	46	910.462	1.821	8.8
8	3318.666	6.638	31.1	47	908.509	1.817	6.9
9	3140.931	6.283	58.2	48	867.005	1.734	6.6
10	3132.630	6.266	58.8	49	860.658	1.722	8.8
11	2895.814	5.793	8.3	50	858.216	1.717	6.9
12	2888.978	5.779	8.5	51	853.822	1.708	20.0
13	2878.724	5.758	6.5	52	850.892	1.702	15.8
14	2533.509	5.068	9.3	53	499.330	0.999	54.6
15	2529.603	5.060	16.2	54	495.912	0.992	6.5
16	2528.138	5.057	17.7	55	492.494	0.985	102.4
17	2526.185	5.053	19.6	56	485.169	0.970	53.5
18	2521.302	5.043	6.2	57	274.720	0.550	10.5
19	2511.048	5.023	11.6				
20	2509.095	5.019	12.1				
21	2507.630	5.016	6.0				
22	2489.076	4.979	11.6				
23	2488.099	4.977	10.7				
24	2478.822	4.958	10.3				
25	2019.837	4.040	17.6				
26	2013.001	4.027	52.6				
27	2005.677	4.012	53.5				
28	1998.841	3.998	17.7				
29	1229.798	2.460	20.5				
30	1222.474	2.445	35.8				
31	1214.173	2.429	28.1				
32	1121.888	2.244	10.9				
33	1115.052	2.230	22.7				
34	1107.240	2.215	21.0				
35	1099.916	2.200	7.7				
36	1080.384	2.161	9.2				
37	1078.919	2.158	9.3				
38	1071.107	2.143	25.5				
39	1063.783	2.128	25.2				

JGMM-Char-XI-1575bc2C - Carbon of triol

exp1 s2pul

SAMPLE		DEC. & VT	
date	May 2 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	34
	JasonMCharacteriza~	dof	0
	tion/JGMM-Char-157~	dm	yyy
	5bc2C.fid	dmm	w
ACQUISITION		dmf	10994
sfrq	125.716	dseq	
tn	C13	dres	1.0
at	1.300	homo	n
np	65024	PROCESSING	
sw	25000.0	lb	0.50
fb	14000	wtfile	
bs	4	proc	ft
tpwr	53	fn	not used
pw	6.0	math	f
d1	1.500		
tof	0	werr	
nt	3200	wexp	wft
ct	184	wbs	wft
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-548.0		
wp	24999.2		
vs	602		
sc	0		
wc	250		
hzmm	100.00		
is	500.00		
rfl	16638.9		
rfp	16090.1		
th	9		
ins	100.000		
nm cdc ph			

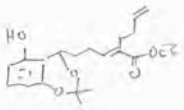
INDEX	FREQUENCY	PPM	HEIGHT
1	21141.568	168.185	13.0
2	19597.379	155.901	43.2
3	17985.288	143.076	32.8
4	17377.988	138.245	26.0
5	16621.152	132.224	25.0
6	16218.320	129.020	36.1
7	16126.767	128.291	45.1
8	16114.560	128.194	581.5
9	16090.146	128.000	601.5
10	16078.702	127.909	26.5
11	16065.732	127.806	594.7
12	14481.870	115.206	32.4
13	14430.753	114.799	24.3
14	13625.851	108.396	56.0
15	8788.052	69.911	36.2
16	7611.600	60.552	33.0
17	4459.134	35.473	32.9
18	4251.614	33.822	48.8
19	3347.531	26.630	37.1
20	3140.012	24.979	36.3
21	1783.505	14.188	41.6



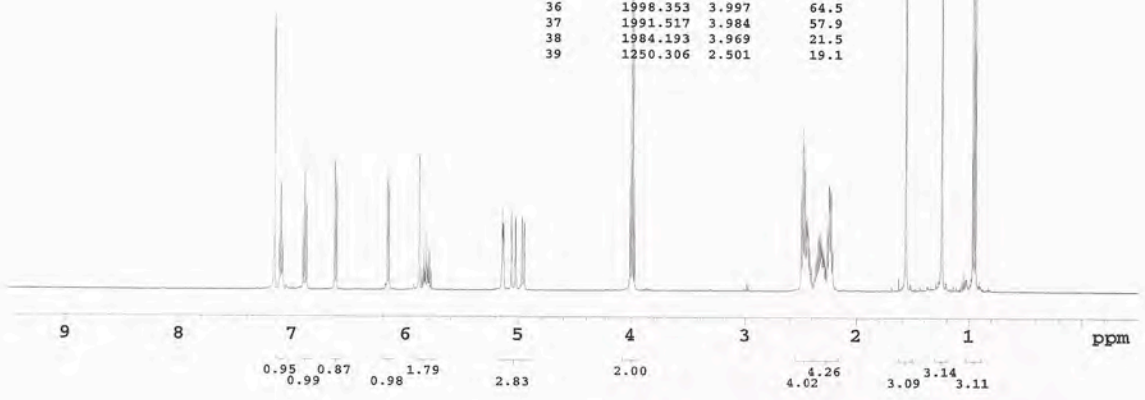
JGMM-XI-1583a2 - Closure to acetonide, N
MR on 500

exp1 s2pul

SAMPLE		DEC. & VT	
date	May 7 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
JasonMCharacteriza~		dof	0
tion/JGMM-Char-XI-~		dm	nnn
1583a2.fid		dmm	c
ACQUISITION		dmf	200
sfrq	499.920	dseq	
tn	H1	dres	1.0
at	1.892	homo	n
np	30272	PROCESSING	
sw	8000.0	wtfile	
fb	4000	proc	ft
bs	4	fn	not used
tpwr	58	math	f
pw	5.5		
d1	2.000	werr	
tof	0	wexp	wft
nt	320	wbs	wft
ct	8	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	151		
sc	35		
wc	215		
hzmm	23.22		
is	33.57		
rfl	5072.3		
rfp	3579.4		
th	7		
ins	2.000		
nm	ph		



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3579.408	7.160	52.6	40	1242.982	2.486	31.2
2	3557.435	7.116	10.7	41	1234.681	2.470	28.0
3	3550.111	7.101	20.4	42	1228.334	2.457	13.5
4	3542.787	7.087	9.7	43	1225.892	2.452	14.5
5	3453.431	6.908	14.0	44	1221.986	2.444	13.6
6	3445.130	6.891	29.1	45	1220.033	2.440	11.2
7	3437.318	6.876	16.4	46	1217.103	2.435	9.5
8	3314.271	6.630	24.2	47	1215.150	2.431	12.0
9	3313.294	6.628	24.8	48	1209.291	2.419	8.4
10	3305.970	6.613	20.9	49	1174.134	2.349	7.8
11	3304.994	6.611	19.7	50	1169.740	2.340	10.3
12	3081.849	6.165	24.3	51	1163.392	2.327	11.4
13	3074.037	6.149	23.2	52	1158.509	2.317	10.2
14	2940.248	5.881	25.4	53	1153.626	2.308	8.8
15	2939.271	5.880	25.6	54	1149.720	2.300	7.2
16	2938.294	5.878	24.9	55	1146.302	2.293	7.5
17	2920.228	5.841	7.8	56	1129.212	2.259	11.9
18	2909.974	5.821	11.1	57	1122.376	2.245	20.3
19	2903.138	5.807	11.4	58	1114.076	2.229	18.8
20	2893.373	5.788	7.8	59	1107.240	2.215	7.5
21	2571.595	5.144	11.7	60	782.044	1.564	151.2
22	2569.154	5.139	15.7	61	622.865	1.246	148.4
23	2565.736	5.132	12.6	62	484.681	0.970	67.7
24	2563.294	5.127	12.7	63	477.357	0.955	140.6
25	2530.580	5.062	14.4	64	470.521	0.941	60.7
26	2528.626	5.058	15.1				
27	2513.490	5.028	13.5				
28	2511.537	5.024	14.0				
29	2484.193	4.969	14.5				
30	2483.216	4.967	13.3				
31	2482.240	4.965	13.8				
32	2473.939	4.949	12.7				
33	2472.962	4.947	12.2				
34	2471.986	4.945	12.8				
35	2005.677	4.012	19.8				
36	1998.353	3.997	64.5				
37	1991.517	3.984	57.9				
38	1984.193	3.969	21.5				
39	1250.306	2.501	19.1				

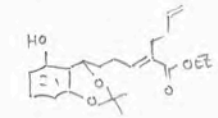


JGMM-XI-1583a2C - Closure to acetonide,
NMR on 500

exp2 s2pul

SAMPLE		DEC. & VT	
date	May 7 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/-	dpwr	34
	JasonMCharacteriza-	dof	0
	tion/JGMM-Char-XI--	dm	yyy
	1583a2C.fid	dmm	w
ACQUISITION		dmf	10994
sfrq	125.716	dseq	
tn	C13	dres	1.0
at	1.300	homo	n
np	65024	PROCESSING	
sw	25000.0	lb	0.50
fb	14000	wtfile	
bs	4	proc	ft
tpwr	53	fn	not used
pw	6.0	math	f
dl	1.500		
tof	0	werr	
nt	1600	wexp	wft
ct	68	wbs	wft
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-523.6		
wp	24999.2		
vs	540		
sc	0		
wc	250		
hzmm	100.00		
is	500.00		
rfl	16614.5		
rfp	16090.1		
th	14		
ins	100.000		
nm cdc ph			

INDEX	FREQUENCY	PPM	HEIGHT
1	21198.785	168.640	19.1
2	19389.856	154.250	33.2
3	19287.622	153.437	29.5
4	18145.502	144.351	37.0
5	17418.420	138.567	47.1
6	16606.653	132.109	32.3
7	16171.777	128.649	56.9
8	16151.178	128.486	32.2
9	16138.208	128.382	499.5
10	16114.557	128.194	523.9
11	16102.350	128.097	20.0
12	16090.143	128.000	539.9
13	14486.444	115.242	47.0
14	13991.296	111.303	39.8
15	13854.730	110.217	63.9
16	13576.257	108.002	48.3
17	12492.883	99.383	63.3
18	8614.099	68.527	56.3
19	7635.248	60.740	43.5
20	4288.232	34.114	62.6
21	4093.683	32.566	51.7
22	3604.639	28.676	74.5
23	3359.735	26.727	49.9
24	3093.469	24.609	56.8
25	2711.237	21.568	77.7
26	1804.864	14.358	59.8

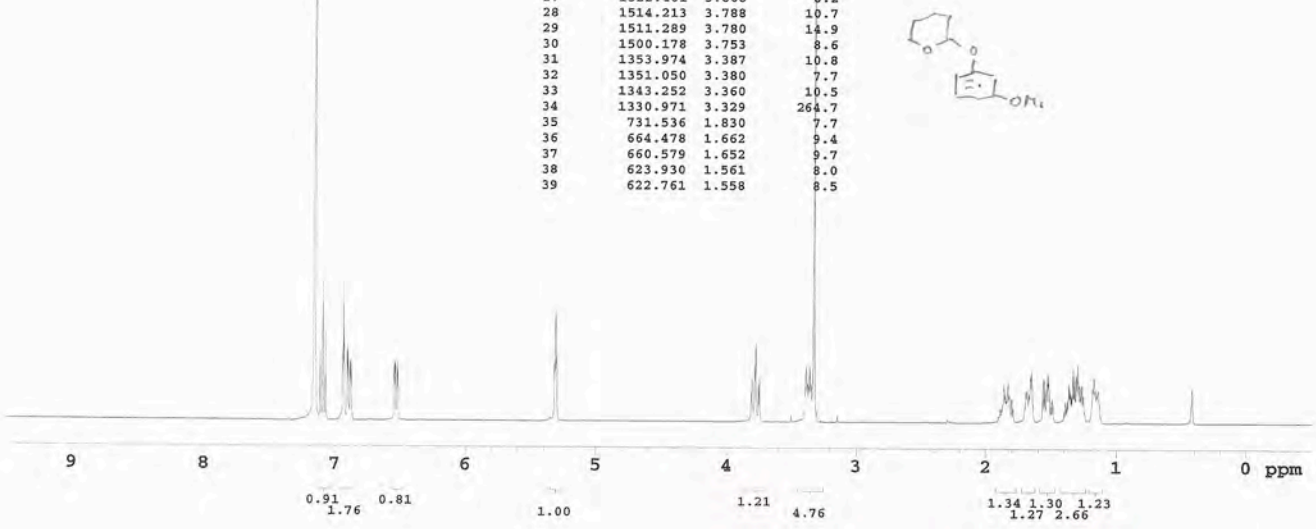


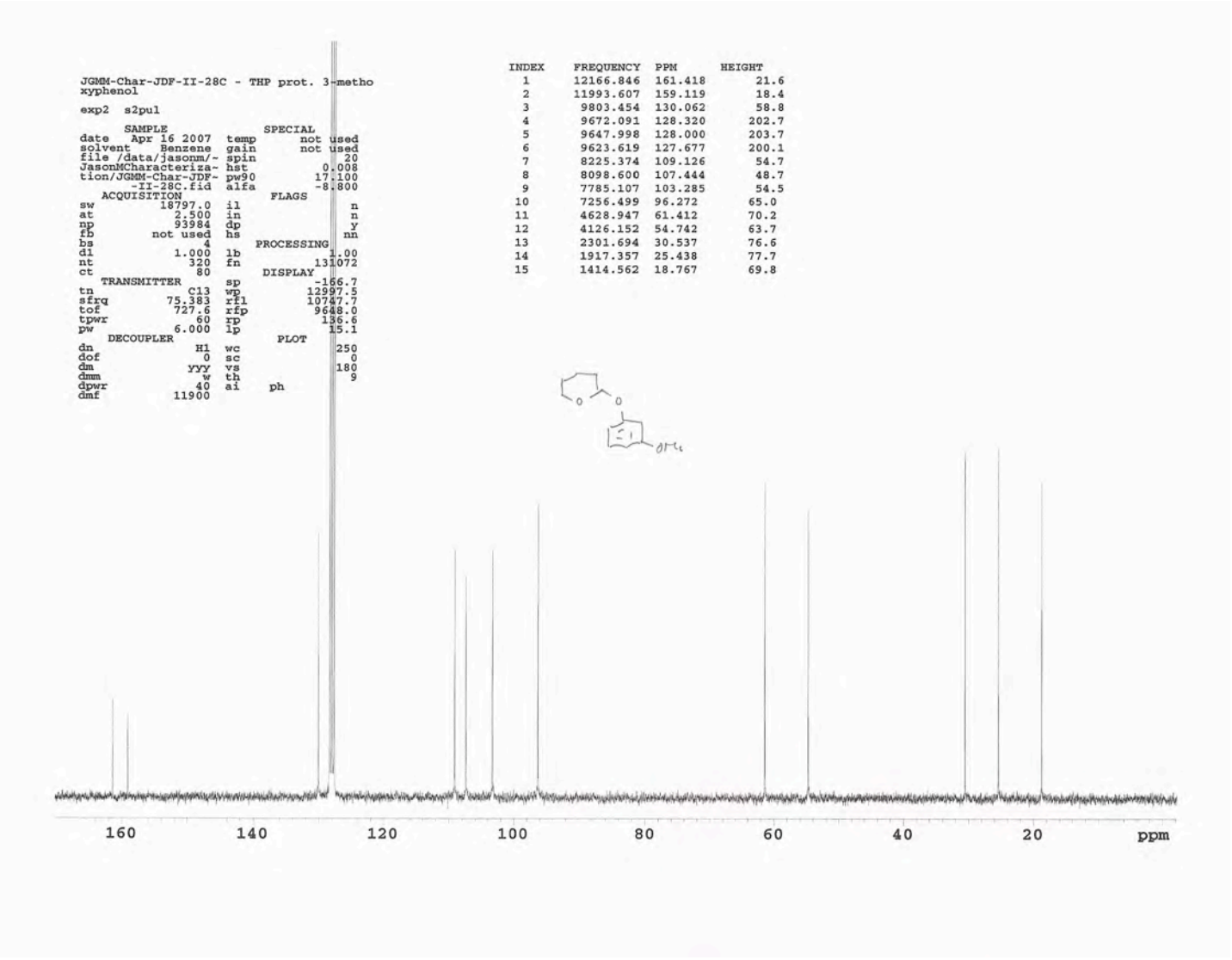
JGMM-Char-JDF-II-28 - THP prot. 3-methoxyphenol

expl s2pul

SAMPLE		SPECIAL	
date	Apr 16 2007	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/~	spin	20
	JasonMCharacteriza~	hst	0.008
	tion/JGMM-Char-JDF~	pw90	6.200
	-II-28.fid	alfa	1.600
ACQUISITION		FLAGS	
sw	6387.7	il	n
at	3.744	in	n
np	47830	dp	y
fb	not used	hs	nn
bs	2	PROCESSING	
d1	1.000	fn	not used
nt	32	DISPLAY	
ct	16	sp	-200.1
TRANSMITTER		wp	3997.6
tn	H1	rfl	3627.2
sfrq	399.780	rfp	2862.4
tof	399.5	rp	-16.3
tpwr	53	lp	-7.1
pw	6.450	is	500
DECOUPLER		PLOT	
dn		wc	250
dof	0	sc	0
dm	nnn	vs	57
dmm	c	th	8
dpwr	33	ai	ph
dmf	29412		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2862.601	7.160	108.0	40	619.642	1.550	7.9
2	2845.056	7.117	13.1	41	612.429	1.532	7.6
3	2836.869	7.096	29.1	42	611.064	1.529	9.4
4	2828.682	7.076	16.6	43	609.310	1.524	7.9
5	2776.438	6.945	13.0	44	533.089	1.333	10.4
6	2774.294	6.940	26.3	45	528.995	1.323	8.9
7	2771.955	6.934	17.9	46	523.927	1.311	8.8
8	2761.233	6.907	13.2	47	522.952	1.308	9.2
9	2760.258	6.904	14.5	48	519.833	1.300	11.1
10	2758.894	6.901	12.8	49	469.929	1.175	8.7
11	2757.919	6.899	10.9				
12	2752.851	6.886	11.1				
13	2752.071	6.884	11.5				
14	2750.706	6.881	10.8				
15	2749.732	6.878	8.9				
16	2618.733	6.550	10.5				
17	2617.758	6.548	11.2				
18	2616.199	6.544	12.2				
19	2615.419	6.542	10.8				
20	2610.351	6.530	10.2				
21	2609.571	6.528	10.4				
22	2608.012	6.524	11.3				
23	2607.232	6.522	9.6				
24	2126.319	5.319	11.1				
25	2123.395	5.311	21.0				
26	2120.471	5.304	12.3				
27	1522.401	3.808	8.2				
28	1514.213	3.788	10.7				
29	1511.289	3.780	14.9				
30	1500.178	3.753	8.6				
31	1353.974	3.387	10.8				
32	1351.050	3.380	7.7				
33	1343.252	3.360	10.5				
34	1330.971	3.329	264.7				
35	731.536	1.830	7.7				
36	664.478	1.662	9.4				
37	660.579	1.652	9.7				
38	623.930	1.561	8.0				
39	622.761	1.558	8.5				

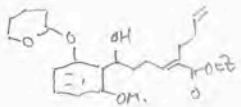



JGMM-Char-JDF-II-28C - THP prot. 3-metho
xyphenol
exp2 s2pul
SAMPLE
date Apr 16 2007
solvent Benzene
file /data/jasonm/-
JasonMCharacteriza-
tion/JGMM-Char-JDF-
-II-28C.fid
ACQUISITION
sw 18797.0
at 2.500
np 93984
fb not used
bs 4
d1 1.000
nt 320
ct 80
TRANSMITTER
tn C13
sfrq 75.383
tof 727.6
tpwr 60
pw 6.000
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 40
dmf 11900
SPECIAL
temp not used
gain not used
spin 20
hst 0.008
pw90 17.100
alfa -8.800
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn 131072
DISPLAY
sp -166.7
wp 12997.5
rfl 10747.7
rfp 9648.0
rp 136.6
lp 15.1
PLOT
wc 250
sc 0
vs 180
th 9
ai ph
INDEX FREQUENCY PPM HEIGHT
1 12166.846 161.418 21.6
2 11993.607 159.119 18.4
3 9803.454 130.062 58.8
4 9672.091 128.320 202.7
5 9647.998 128.000 203.7
6 9623.619 127.677 200.1
7 8225.374 109.126 54.7
8 8098.600 107.444 48.7
9 7785.107 103.285 54.5
10 7256.499 96.272 65.0
11 4628.947 61.412 70.2
12 4126.152 54.742 63.7
13 2301.694 30.537 76.6
14 1917.357 25.438 77.7
15 1414.562 18.767 69.8
O
O
OMe
160
140
120
100
80
60
40
20
ppm

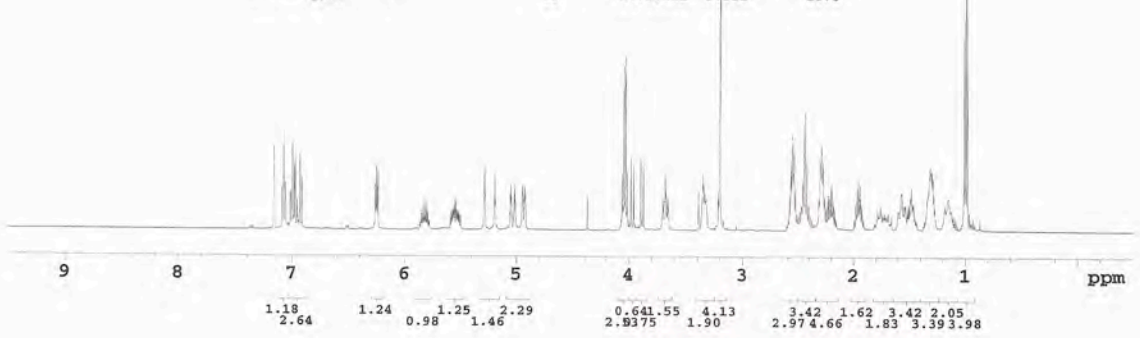
JGMM-XI-1572b - THP/OMe o-lithiation/aldol, product spot

expl s2pul

SAMPLE		DEC. & VT	
date	Apr 23 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
	JasonMCharacteriza-	dof	0
	tion/JGMM-Char-XI--	dm	nnn
	1572b.fid	dmm	c
ACQUISITION		dmf	200
sfrq	499.920	dseq	
tn	H1	dres	1.0
at	1.892	homo	n
np	30272	temp	22.0
sw	8000.0	PROCESSING	
fb	4000	wtfile	
bs	4	proc	ft
tpwr	58	fn	not used
pw	5.5	math	f
dl	0		
tof	0	werr	
nt	320	wexp	wft
ct	36	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	162		
sc	35		
wc	215		
hzmm	23.22		
is	1754.63		
rfl	5072.3		
rfp	3579.4		
th	8		
ins	1.000		
nm	ph		



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3579.408	7.160	16.7	40	1672.669	3.346	8.8
2	3544.740	7.091	9.0	41	1601.869	3.204	162.2
3	3536.927	7.075	18.9	42	1286.439	2.573	11.2
4	3529.603	7.060	9.3	43	1283.509	2.567	13.5
5	3499.818	7.001	16.5	44	1278.626	2.558	18.5
6	3498.353	6.998	18.5	45	1275.697	2.552	11.3
7	3492.005	6.985	13.8	46	1271.302	2.543	15.7
8	3490.052	6.981	12.4	47	1265.443	2.531	8.5
9	3486.146	6.973	12.7	48	1232.240	2.465	9.8
10	3484.681	6.971	15.4	49	1224.916	2.450	20.4
11	3464.662	6.930	16.7	50	1217.103	2.435	23.1
12	3456.849	6.915	10.1	51	1209.779	2.420	13.4
13	3130.677	6.262	9.1	52	1149.232	2.299	13.6
14	3129.701	6.260	8.7	53	1143.373	2.287	16.8
15	3126.283	6.254	12.7	54	1137.025	2.274	13.2
16	3122.865	6.247	9.1	55	1099.427	2.199	9.1
17	3121.400	6.244	8.4	56	982.728	1.966	8.4
18	3117.982	6.237	11.7	57	977.357	1.955	9.6
19	2641.419	5.284	12.5	58	969.544	1.939	8.8
20	2596.009	5.193	11.2	59	742.005	1.484	8.3
21	2525.209	5.051	9.4	60	660.462	1.321	10.5
22	2523.744	5.048	8.5	61	658.021	1.316	12.3
23	2508.119	5.017	8.9	62	656.068	1.312	11.1
24	2506.654	5.014	8.0	63	653.626	1.307	11.4
25	2472.962	4.947	8.5	64	651.673	1.304	10.3
26	2471.986	4.945	8.6	65	649.232	1.299	11.4
27	2462.709	4.926	8.4	66	645.326	1.291	10.0
28	2461.732	4.924	7.9	67	505.189	1.011	40.6
29	2030.580	4.062	10.8	68	502.748	1.006	8.3
30	2023.744	4.048	31.5	69	498.353	0.997	84.9
31	2016.419	4.034	33.4	70	491.029	0.982	40.8
32	2009.095	4.019	11.8				
33	1991.029	3.983	14.0				
34	1979.310	3.959	12.7				
35	1948.548	3.898	14.2				
36	1936.830	3.874	14.8				
37	1838.685	3.678	11.6				
38	1835.755	3.672	8.2				
39	1675.111	3.351	10.8				

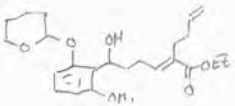


JGMM-XI-1572bC

exp2 s2pul

SAMPLE		DEC. & VT	
date	Apr 25 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	34
	JasonMCharacteriza~	dof	0
	tion/JGMM-Char-XI--	dm	yyy
	1572bC.fid	dmm	w
ACQUISITION		dmf	10994
sfrq	125.716	dseq	
tn	C13	dres	1.0
at	1.300	homo	n
np	65024	temp	22.0
sw	25000.0	PROCESSING	
fb	14000	lb	0.50
bs	4	wtfile	
tpwr	53	proc	ft
pw	6.0	fn	not used
d1	1.500	math	f
tof	0		
nt	3200	werr	
ct	68	wexp	wft
alock	n	wbs	wft
gain	not used	wnt	
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-522.1		
wp	24999.2		
vs	383		
sc	0		
wc	250		
hzmm	100.00		
is	500.00		
rfl	16613.0		
rfp	16090.1		
th	12		
ins	100.000		
nm cdc ph			

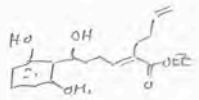
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	21058.404	167.523	26.440		3848.779	30.618	65.5
2	19905.603	158.353	30.941		3391.778	26.982	55.9
3	19901.025	158.316	22.942		3387.964	26.952	52.0
4	19605.768	155.967	20.343		3297.174	26.230	40.8
5	19541.681	155.458	23.244		3285.730	26.139	60.5
6	17985.284	143.076	63.145		3201.806	25.471	59.8
7	17983.758	143.064	50.146		3195.703	25.422	51.5
8	17428.338	138.646	46.147		2415.216	19.213	38.1
9	17426.050	138.627	33.548		2378.595	18.922	57.6
10	16671.502	132.625	29.849		1824.701	14.516	96.8
11	16666.925	132.588	28.2				
12	16168.725	128.625	49.9				
13	16158.044	128.540	58.3				
14	16150.415	128.479	27.9				
15	16138.208	128.382	367.9				
16	16114.557	128.194	371.0				
17	16103.113	128.103	16.2				
18	16090.143	128.000	383.0				
19	15279.138	121.548	16.7				
20	15250.909	121.324	19.2				
21	14475.000	115.151	72.1				
22	13688.409	108.894	46.6				
23	13643.396	108.536	57.3				
24	13231.408	105.258	44.8				
25	13213.098	105.113	51.5				
26	12231.195	97.301	35.7				
27	12091.577	96.191	47.9				
28	8530.176	67.859	44.7				
29	8524.835	67.817	54.2				
30	7790.124	61.972	44.8				
31	7749.688	61.650	50.3				
32	7581.079	60.309	89.2				
33	6953.943	55.320	68.0				
34	6952.417	55.308	79.5				
35	4739.129	37.701	48.5				
36	4735.315	37.670	61.6				
37	4290.521	34.132	76.4				
38	4288.232	34.114	49.5				
39	3853.357	30.654	54.3				



JGMM-Char-XI-1577 - THP/OMe deprot.

expl s2pul

SAMPLE		DEC. & VT	
date	May 1 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
JasonMCharacteriza~		dof	0
tion/JGMM-Char-157~		dm	nnn
	7.fid	dmm	c
ACQUISITION		dmf	200
sfrq	499.920	dseq	
tn	H1	dres	1.0
at	1.892	homo	n
np	30272	PROCESSING	
sw	8000.0	wtfile	
fb	4000	proc	ft
bs	4	fn	not used
tpwr	58	math	f
pw	5.5		
d1	0	werr	
tof	0	wexp	wft
nt	320	wbs	wft
ct	16	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	162		
sc	35		
wc	215		
hzmm	23.22		
is	2934.32		
rfl	5072.8		
rfp	3579.4		
th	4		
ins	3.000		
nm	ph		



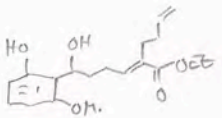
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	4531.556	9.065	41.4	40	1206.849	2.414	21.1
2	3579.408	7.160	17.7	41	1111.146	2.223	8.5
3	3497.377	6.996	9.8	42	1104.798	2.210	23.6
4	3489.076	6.979	21.2	43	1097.474	2.195	38.7
5	3480.775	6.963	12.1	44	1090.150	2.181	32.0
6	3452.943	6.907	8.6	45	1082.826	2.166	10.6
7	3445.619	6.892	17.2	46	961.732	1.924	5.8
8	3437.806	6.877	8.5	47	954.896	1.910	6.9
9	3390.931	6.783	16.5	48	947.572	1.895	8.5
10	3382.630	6.766	14.6	49	940.248	1.881	6.4
11	3059.388	6.120	18.6	50	878.236	1.757	5.2
12	3051.087	6.103	18.2	51	872.865	1.746	6.6
13	2888.002	5.777	6.3	52	864.564	1.729	6.2
14	2881.166	5.763	6.5	53	805.970	1.612	10.6
15	2870.912	5.743	4.6	54	494.935	0.990	35.5
16	2617.982	5.237	5.0	55	487.611	0.975	81.8
17	2613.587	5.228	9.5	56	481.263	0.963	32.6
18	2609.193	5.219	9.8	57	449.037	0.898	4.7
19	2605.287	5.211	9.4				
20	2600.892	5.203	5.0				
21	2518.373	5.038	9.6				
22	2516.908	5.035	9.8				
23	2501.283	5.003	9.2				
24	2499.818	5.000	9.1				
25	2479.310	4.959	10.1				
26	2478.334	4.957	8.9				
27	2470.033	4.941	7.0				
28	2469.056	4.939	9.7				
29	2468.080	4.937	8.9				
30	2467.103	4.935	7.6				
31	2007.630	4.016	11.8				
32	2000.794	4.002	32.2				
33	1993.470	3.988	37.4				
34	1986.146	3.973	10.9				
35	1651.185	3.303	162.0				
36	1433.412	2.867	13.6				
37	1429.505	2.859	12.9				
38	1221.986	2.444	15.6				
39	1214.662	2.430	27.9				

JGMM-Char-XI-1577C - THP/OMe deprot.

exp2 s2pul

SAMPLE		DEC. & VT	
date	May 1 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	34
	JasonMCharacteriza~	dof	0
	tion/JGMM-Char-XI--	dm	yyy
	1577.fid	dmm	w
ACQUISITION		dmf	10994
sfrq	125.716	dseq	
tn	C13	dres	1.0
at	1.300	homo	n
np	65024	PROCESSING	
sw	25000.0	lb	0.50
fb	14000	wtfile	
bs	4	proc	ft
tpwr	53	fn	not used
pw	6.0	math	f
d1	1.500		
tof	0	werr	
nt	3200	wexp	wft
ct	80	wbs	wft
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-523.6		
wp	24999.2		
vs	320		
sc	0		
wc	250		
hzmm	100.00		
is	500.00		
rfl	16614.5		
rfp	16090.1		
th	11		
ins	100.000		
nm cdc ph			

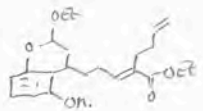
INDEX	FREQUENCY	PPM	HEIGHT
1	21109.521	167.930	25.6
2	19904.077	158.341	34.1
3	19724.786	156.914	24.4
4	17967.737	142.937	61.1
5	17406.976	138.476	40.2
6	16649.377	132.449	42.8
7	16242.731	129.214	59.4
8	16151.178	128.486	21.4
9	16138.971	128.388	299.4
10	16114.557	128.194	316.5
11	16103.113	128.103	13.6
12	16090.143	128.000	319.7
13	14590.204	116.068	40.2
14	14494.836	115.309	49.1
15	13965.356	111.097	67.1
16	12829.340	102.060	53.3
17	8801.782	70.020	51.9
18	7613.123	60.564	45.5
19	6940.973	55.217	78.5
20	4507.196	35.856	57.9
21	4273.737	33.998	81.7
22	3376.520	26.861	54.3
23	3172.815	25.240	68.0
24	1813.257	14.425	64.9



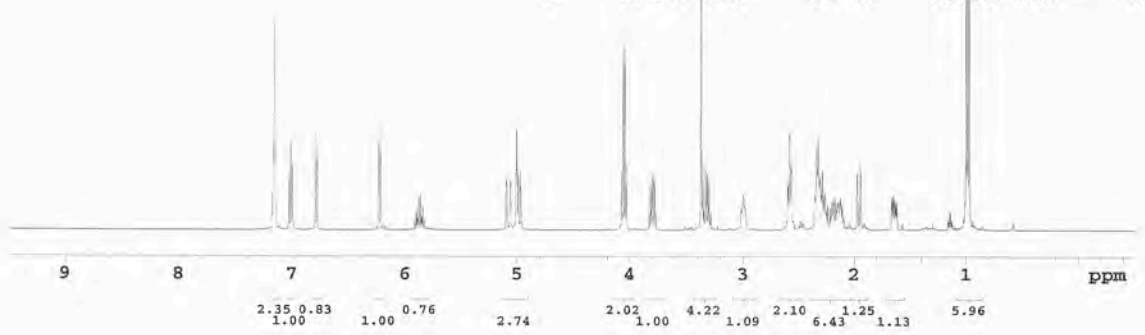
JGMM-XI-Char-1579 - Isocynate/EVE rxn

expl s2pul

SAMPLE		DEC. & VT	
date	May 2 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/-	dpwr	30
	JasonMCharacteriza-	dof	0
	tion/JGMM-Char-XI--	dm	nnn
	1579.fid	dmm	c
ACQUISITION		dmf	200
sfrq	499.920	dseq	
tn	H1	dres	1.0
at	1.892	homo	n
np	30272	PROCESSING	
sw	8000.0	wtfile	
fb	4000	proc	ft
bs	4	fn	not used
tpwr	58	math	f
pw	5.5		
d1	2.000	werr	
tof	0	wexp	wft
nt	320	wbs	wft
ct	12	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	158		
sc	35		
wc	215		
hzmm	23.22		
is	33.57		
rfl	5072.3		
rfp	3579.4		
th	4		
ins	1.000		
nm	ph		



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM
1	3591.126	7.183	7.5	40	1890.443	3.782	9.3	79	1088.685	2.178
2	3583.802	7.169	16.6	41	1889.466	3.780	10.6	80	1087.709	2.176
3	3579.408	7.160	40.3	42	1685.365	3.371	158.2	81	1081.361	2.163
4	3515.443	7.032	11.1	43	1678.529	3.358	12.2	82	1075.501	2.151
5	3507.142	7.015	22.8	44	1666.322	3.333	12.1	83	1071.595	2.144
6	3499.330	7.000	12.8	45	1664.857	3.330	5.5	84	1066.712	2.134
7	3397.279	6.796	18.6	46	1659.974	3.320	9.9	85	1063.783	2.128
8	3388.978	6.779	16.3	47	1658.998	3.319	10.8	86	1060.365	2.121
9	3117.005	6.235	20.9	48	1657.533	3.316	9.5	87	1056.947	2.114
10	3108.705	6.218	19.3	49	1656.556	3.314	10.9	88	987.123	1.975
11	2949.525	5.900	4.6	50	1652.162	3.305	4.7	89	985.169	1.971
12	2939.271	5.880	6.9	51	1649.720	3.300	9.9	90	983.705	1.968
13	2932.435	5.866	6.9	52	1500.306	3.001	6.8	91	972.962	1.946
14	2922.181	5.845	4.8	53	1498.353	2.997	6.6	92	971.009	1.942
15	2547.181	5.095	9.9	54	1493.959	2.988	4.8	93	969.544	1.939
16	2546.205	5.093	9.6	55	1302.552	2.606	8.5	94	832.337	1.665
17	2545.228	5.091	9.4	56	1299.623	2.600	9.9	95	828.919	1.658
18	2530.091	5.061	9.9	57	1293.763	2.588	18.5	96	825.501	1.651
19	2529.115	5.059	9.3	58	1292.298	2.585	17.9	97	822.084	1.644
20	2528.138	5.057	8.9	59	1289.369	2.579	6.2	98	818.177	1.637
21	2526.673	5.054	4.4	60	1286.439	2.573	12.5	99	814.759	1.630
22	2504.212	5.009	11.7	61	1284.486	2.569	11.9	100	811.341	1.623
23	2501.771	5.004	19.4	62	1177.552	2.355	6.9	101	807.923	1.616
24	2498.841	4.999	11.7	63	1176.576	2.354	6.9	102	505.189	1.011
25	2495.423	4.992	8.6	64	1170.716	2.342	15.9	103	503.236	1.007
26	2494.447	4.990	10.9	65	1162.416	2.325	17.7	104	500.306	1.001
27	2492.982	4.987	10.5	66	1158.021	2.316	8.9	105	496.400	0.993
28	2492.005	4.985	8.4	67	1155.091	2.311	10.4	106	492.982	0.986
29	2485.169	4.971	8.6	68	1151.673	2.304	9.7	107	486.146	0.972
30	2484.193	4.969	11.4	69	1148.255	2.297	7.1			
31	2483.216	4.967	10.0	70	1143.373	2.287	11.8			
32	2037.416	4.076	11.6	71	1138.001	2.276	6.5			
33	2029.603	4.060	35.7	72	1132.630	2.266	7.3			
34	2022.279	4.045	34.7	73	1130.677	2.262	6.5			
35	2015.443	4.032	12.6	74	1119.935	2.240	4.8			
36	1907.044	3.815	8.5	75	1109.193	2.219	4.4			
37	1906.068	3.813	9.1	76	1101.380	2.203	5.6			
38	1899.232	3.799	10.8	77	1095.521	2.191	6.2			
39	1896.791	3.794	10.7	78	1094.544	2.189	6.0			

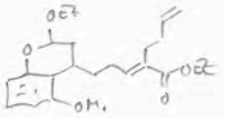


JGMM-Char-XI-1579C - Carbon of isocyanate/EVE rxn

exp2 s2pul

SAMPLE		DEC. & VT	
date	May 1 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	34
	JasonMCharacteriza~	dof	0
	tion/JGMM-Char-XI--	dm	yyy
	1579C.fid	dmm	w
ACQUISITION		dmf	10994
sfrq	125.716	dseq	
tn	C13	dres	1.0
at	1.300	homo	n
np	65024	PROCESSING	
sw	25000.0	lb	0.50
fb	14000	wtfile	
bs	4	proc	ft
tpwr	53	fn	not used
pw	6.0	math	f
d1	1.500		
tof	0	werr	
nt	3200	wexp	wft
ct	8	wbs	wft
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-545.0		
wp	24999.2		
vs	140		
sc	0		
wc	250		
hzmm	100.00		
is	500.00		
rfl	16635.9		
rfp	16090.1		
th	10		
ins	100.000		
nm cdc ph			

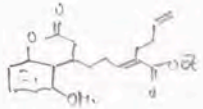
INDEX	FREQUENCY	PPM	HEIGHT
1	21036.282	167.347	25.5
2	19868.222	158.055	26.9
3	19203.701	152.769	20.0
4	18015.042	143.313	49.1
5	17409.268	138.494	34.2
6	16604.367	132.091	34.2
7	16114.560	128.194	138.2
8	16090.146	128.000	138.6
9	16066.494	127.812	140.4
10	16043.606	127.630	53.7
11	14545.193	115.710	33.1
12	14454.403	114.987	40.4
13	13889.828	110.496	45.9
14	12950.650	103.025	39.8
15	12257.138	97.508	36.9
16	8053.341	64.066	42.1
17	7558.957	60.133	39.8
18	6915.799	55.016	53.5
19	4275.265	34.011	51.2
20	4142.514	32.954	47.3
21	3595.486	28.603	41.1
22	3506.222	27.893	43.8
23	3391.018	26.976	52.1
24	3365.078	26.770	51.2
25	1931.515	15.366	46.5
26	1802.578	14.340	44.3



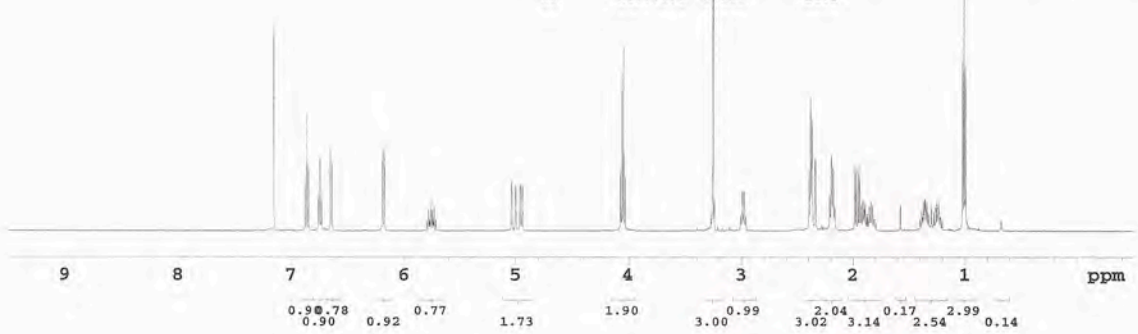
JGMM-XI-1587a - Jones oxidation to lacto
ne

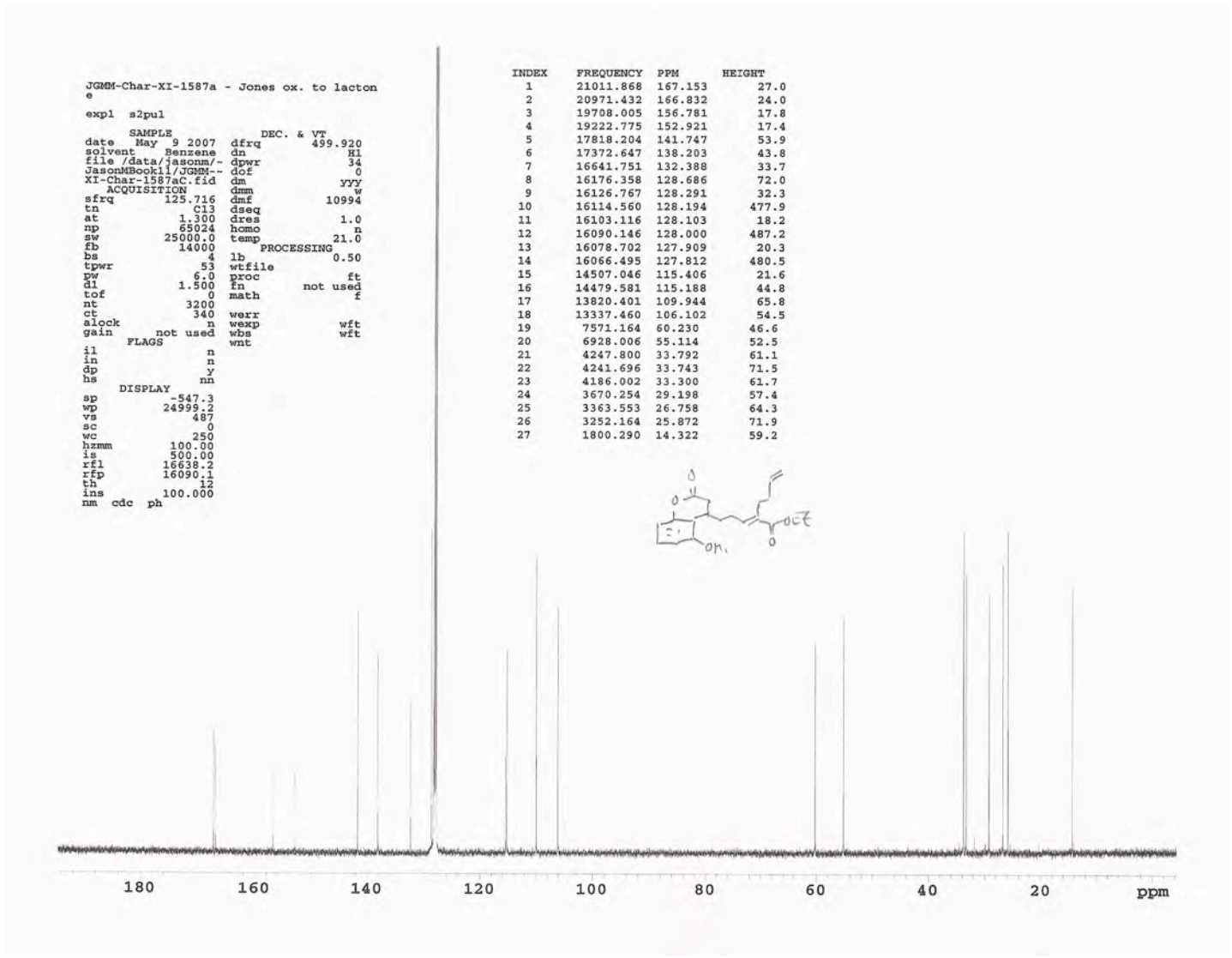
expl s2pul

SAMPLE		DEC. & VT	
date	May 9 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/-	dpwr	30
	JasonMCharacteriza-	dof	0
	tion/JGMM-Char-XI--	dm	nnn
	1587a.fid	dmm	c
ACQUISITION		dmf	200
sfrq	499.920	dseq	
tn	H1	dres	1.0
at	1.892	homo	n
np	30272	temp	21.0
sw	8000.0	PROCESSING	
fb	4000	wtfile	
bs	4	proc	ft
tpwr	58	fn	not used
pw	5.5	math	f
d1	2.000		
tof	0	werr	
nt	320	wexp	wft
ct	8	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	144		
sc	35		
wc	215		
hzmm	23.22		
is	1261.20		
rfl	5072.8		
rfp	3579.4		
th	4		
ins	3.000		
nm	ph		



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3579.408	7.160	39.6	40	1090.150	2.181	12.3
2	3439.759	6.881	10.5	41	1083.314	2.167	4.5
3	3431.459	6.864	22.7	42	992.494	1.985	12.2
4	3423.158	6.847	12.7	43	986.146	1.973	12.4
5	3380.677	6.762	8.0	44	976.869	1.954	12.2
6	3373.353	6.748	14.8	45	970.521	1.941	12.8
7	3366.029	6.733	7.9	46	961.732	1.924	5.0
8	3326.966	6.655	16.1	47	955.384	1.911	6.0
9	3318.666	6.638	13.3	48	952.455	1.905	4.2
10	3094.544	6.190	16.1	49	949.037	1.898	4.1
11	3086.244	6.174	15.4	50	946.107	1.893	5.7
12	2889.955	5.781	4.2	51	928.041	1.856	4.5
13	2880.189	5.761	6.5	52	927.064	1.854	4.4
14	2873.353	5.748	6.6	53	925.599	1.852	4.4
15	2863.099	5.727	4.7	54	919.252	1.839	5.8
16	2517.884	5.037	9.4	55	911.439	1.823	5.2
17	2516.419	5.034	9.6	56	786.439	1.573	5.0
18	2500.794	5.002	8.8	57	691.712	1.384	3.9
19	2499.330	4.999	8.9	58	684.877	1.370	5.7
20	2480.287	4.961	8.8	59	681.947	1.364	4.1
21	2479.310	4.959	8.9	60	678.041	1.356	6.1
22	2470.521	4.942	8.8	61	675.111	1.350	6.0
23	2469.056	4.939	8.3	62	671.205	1.343	4.3
24	2034.486	4.070	11.8	63	668.275	1.337	5.6
25	2027.650	4.056	30.7	64	649.232	1.299	5.3
26	2020.326	4.041	35.1	65	632.142	1.264	4.6
27	2013.490	4.028	10.6	66	631.166	1.263	4.6
28	1625.794	3.252	143.6	67	629.212	1.259	4.2
29	1619.447	3.239	6.1	68	624.818	1.250	6.2
30	1495.912	2.992	7.6	69	622.865	1.246	4.7
31	1488.587	2.978	7.6	70	621.888	1.244	4.5
32	1197.572	2.396	11.7	71	615.541	1.231	5.5
33	1189.759	2.380	25.8	72	510.072	1.020	32.3
34	1185.365	2.371	14.1	73	505.189	1.011	6.6
35	1182.435	2.365	21.2	74	502.748	1.006	76.4
36	1169.252	2.339	14.0	75	498.841	0.998	6.2
37	1167.787	2.336	13.4	76	495.912	0.992	31.4
38	1104.798	2.210	7.0				
39	1097.474	2.195	14.5				

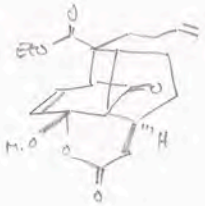



JGMM-Char-XI-1587a - Jones ox. to lacton
e
exp1 s2pul
SAMPLE
date May 9 2007
solvent Benzene
file /data/jasonm/-
JasonMBook11/JGMM--
XI-Char-1587aC.fid
ACQUISITION
sfrq 125.716
tn C13
at 1.300
np 65024
sw 25000.0
fb 14000
bs 4
tpwr 53
pw 6.0
d1 1.500
tof 0
nt 3200
ct 340
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -547.3
wp 24999.2
vs 487
sc 0
wc 250
hzmm 100.00
is 500.00
rfl 16638.2
rfp 16090.1
th 12
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.920
dn H1
dpwr 34
dof 0
dm yyy
dmm w
dmf 10994
dseq
dres 1.0
homo n
temp 21.0
PROCESSING
lb 0.50
wtfile
proc ft
fn not used
math f
werr
wexp wft
wbs wft
wnt
INDEX FREQUENCY PPM HEIGHT
1 21011.868 167.153 27.0
2 20971.432 166.832 24.0
3 19708.005 156.781 17.8
4 19222.775 152.921 17.4
5 17818.204 141.747 53.9
6 17372.647 138.203 43.8
7 16641.751 132.388 33.7
8 16176.358 128.686 72.0
9 16126.767 128.291 32.3
10 16114.560 128.194 477.9
11 16103.116 128.103 18.2
12 16090.146 128.000 487.2
13 16078.702 127.909 20.3
14 16066.495 127.812 480.5
15 14507.046 115.406 21.6
16 14479.581 115.188 44.8
17 13820.401 109.944 65.8
18 13337.460 106.102 54.5
19 7571.164 60.230 46.6
20 6928.006 55.114 52.5
21 4247.800 33.792 61.1
22 4241.696 33.743 71.5
23 4186.002 33.300 61.7
24 3670.254 29.198 57.4
25 3363.553 26.758 64.3
26 3252.164 25.872 71.9
27 1800.290 14.322 59.2
180
160
140
120
100
80
60
40
20
ppm

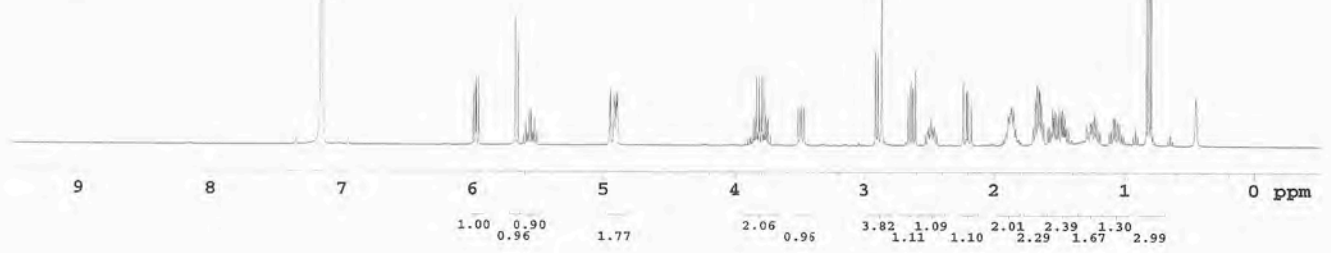
JGMM-XI-164la - PIDA/hexaFisopropanol ox dearomatization, quick rxn time

expl s2pul

SAMPLE		SPECIAL	
date	Jun 24 2007	temp	21.0
solvent	Benzene	gain	not used
file	/data/jasonm/~	spin	20
JasonMBook11/JGMM-~		hst	0.008
	XI-164la.fid	pw90	6.200
ACQUISITION		alfa	1.600
sw	6387.7	FLAGS	
at	3.744	il	n
np	47830	in	n
fb	not used	dp	y
bs	2	hs	nn
dl	1.000	PROCESSING	
nt	320	fn	not used
ct	8	DISPLAY	
TRANSMITTER		sp	-200.1
tn	H1	wp	3997.6
sfrq	399.780	rf1	3627.8
tof	399.5	rfp	2862.4
tpwr	53	rp	174.1
pw	6.450	lp	5.3
DECOUPLER		is	500
dn		PLOT	
dof	0	wc	250
dm	nnn	sc	0
dmm	c	vs	55
dpwr	33	th	4
dmf	29412	ai ph	



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM
1	2862.406	7.160	217.6	40	1146.560	2.868	160.2	79	487.669	1.22(
2	2397.673	5.998	11.5	41	1065.270	2.665	9.6	80	436.010	1.091
3	2390.460	5.979	11.8	42	1057.473	2.645	12.6	81	430.162	1.076
4	2387.926	5.973	13.5	43	1050.260	2.627	11.3	82	422.754	1.057
5	2380.714	5.955	13.3	44	1042.268	2.607	14.5	83	416.906	1.043
6	2268.624	5.675	25.3	45	993.923	2.486	5.2	84	333.667	0.835
7	2258.877	5.650	21.9	46	894.894	2.238	12.5	85	328.599	0.822
8	2236.069	5.593	4.7	47	884.758	2.213	10.7	86	326.650	0.817
9	2225.738	5.567	7.0	48	879.689	2.200	10.8	87	319.437	0.799
10	2219.110	5.551	7.3	49	869.747	2.176	9.4	88	180.836	0.452
11	2208.778	5.525	5.6	50	756.293	1.892	6.0			
12	1979.726	4.952	9.4	51	755.124	1.889	5.9			
13	1978.166	4.948	10.8	52	752.590	1.883	4.7			
14	1976.607	4.944	4.7	53	749.666	1.875	6.6			
15	1968.029	4.923	10.0	54	745.962	1.866	7.6			
16	1966.665	4.919	9.1	55	744.402	1.862	7.3			
17	1962.571	4.909	8.3	56	743.038	1.859	5.4			
18	1961.012	4.905	10.4	57	739.139	1.849	7.1			
19	1959.257	4.901	8.4	58	737.969	1.846	5.9			
20	1957.893	4.897	10.1	59	673.055	1.684	9.4			
21	1956.528	4.894	8.0	60	667.402	1.669	11.9			
22	1544.819	3.864	6.1	61	660.969	1.653	11.3			
23	1541.115	3.855	4.5	62	659.019	1.648	10.4			
24	1537.606	3.846	6.4	63	655.510	1.640	8.6			
25	1533.902	3.837	13.4	64	647.713	1.620	4.5			
26	1526.884	3.819	13.6	65	621.591	1.555	7.4			
27	1524.740	3.814	5.3	66	618.862	1.548	5.5			
28	1519.671	3.801	5.2	67	615.938	1.541	6.9			
29	1517.722	3.796	13.5	68	611.259	1.529	6.6			
30	1510.509	3.778	13.5	69	605.606	1.515	5.7			
31	1506.806	3.769	6.2	70	601.318	1.504	7.4			
32	1503.492	3.761	4.6	71	594.690	1.488	6.9			
33	1499.788	3.752	6.1	72	590.986	1.478	7.1			
34	1407.192	3.520	7.2	73	584.358	1.462	6.3			
35	1399.979	3.502	7.6	74	516.909	1.293	4.4			
36	1395.301	3.490	8.1	75	506.578	1.267	4.6			
37	1388.088	3.472	7.7	76	500.924	1.253	4.8			
38	1165.469	2.915	18.2	77	494.881	1.238	4.9			
39	1158.451	2.898	18.0	78	493.322	1.234	6.3			

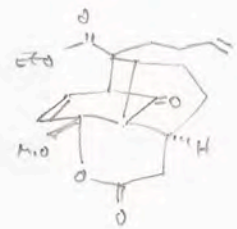


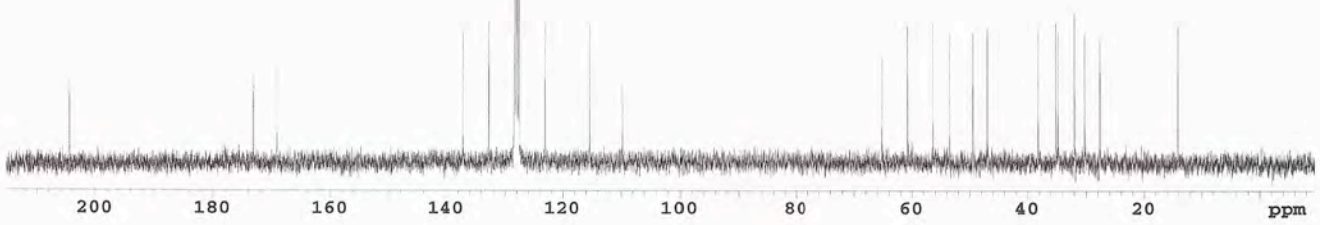
JGMM-XI-1649aC - Carbon of bicycle

expl s2pul

SAMPLE		SPECIAL	
date	Jul 2 2007	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/~	spin	20
	JasonMBook11/JGMM--	hst	0.008
	XI-1649aC.fid	pw90	17.100
ACQUISITION		alfa	-8.800
sw	18797.0	FLAGS	
at	2.500	il	n
np	93984	in	n
fb	not used	dp	y
bs	4	hs	nn
dl	1.000	PROCESSING	
nt	640	lb	1.00
ct	64	fn	131072
TRANSMITTER		DISPLAY	
tn	C13	sp	-711.1
sfrq	75.383	wp	16930.9
tof	727.6	rfl	10748.0
tpwr	60	rfp	9648.0
pw	6.000	rp	136.5
DECOUPLER		lp	22.3
dn	H1	PLOT	
dof	0	wc	250
dm	yyy	sc	0
dmm	w	vs	127
dpwr	40	th	12
dmf	11900	ai ph	

INDEX	FREQUENCY	PPM	HEIGHT
1	15411.059	204.459	16.5
2	13055.412	173.206	17.0
3	12747.655	169.123	18.3
4	10343.822	137.231	25.3
5	10003.654	132.718	27.4
6	9672.378	128.323	335.5
7	9647.998	128.000	335.3
8	9623.906	127.680	333.8
9	9277.141	123.080	27.0
10	8694.611	115.351	26.8
11	8269.831	109.716	15.5
12	4913.471	65.187	20.6
13	4581.908	60.788	26.6
14	4250.058	56.386	27.0
15	4029.494	53.459	25.2
16	3726.039	49.433	24.9
17	3540.180	46.968	25.9
18	2879.062	38.197	25.7
19	2649.033	35.145	27.0
20	2623.506	34.806	25.4
21	2410.686	31.983	28.8
22	2279.609	30.244	24.9
23	2086.006	27.675	23.9
24	1064.929	14.128	26.3



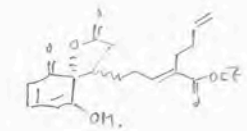


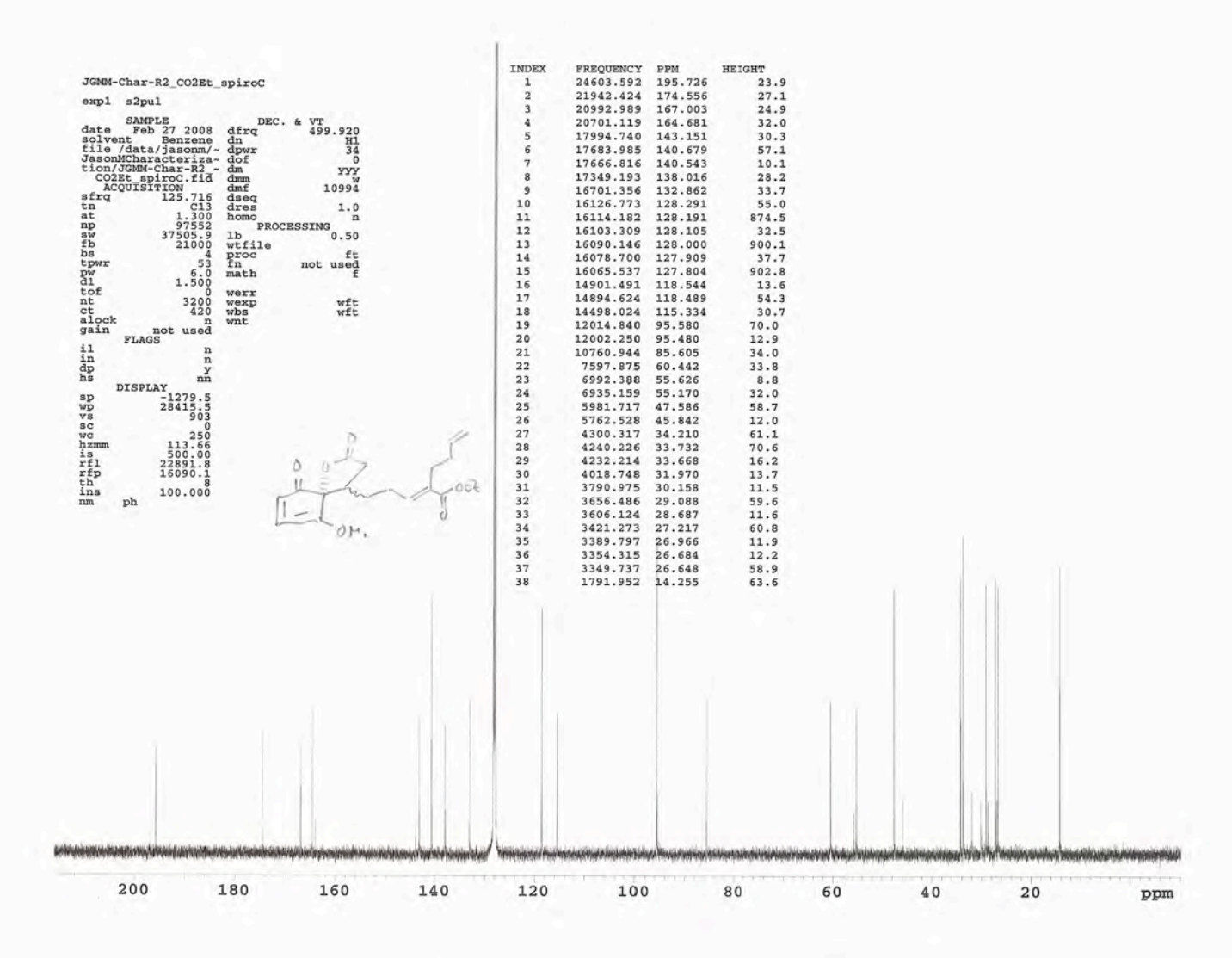
JGMM-XI-1641b - PIDA/hexaFisopropanol ox dearomatization, quick rxn time

exp2 s2pul

SAMPLE		SPECIAL	
date	Jun 24 2007	temp	21.0
solvent	Benzene	gain	not used
file	/data/jasonm/~	spin	20
	JasonMBook11/JGMM--	hst	0.008
	XI-1641b.fid	pw90	6.200
ACQUISITION		alfa	1.600
sw	6387.7	FLAGS	
at	3.744	il	n
np	47830	in	n
fb	not used	dp	y
bs	2	hs	nn
d1	1.000	PROCESSING	
nt	320	fn	not used
ct	36	DISPLAY	
TRANSMITTER		sp	-200.1
tn	H1	wp	3997.6
sfrq	399.780	rfl	3627.8
tof	399.5	rfp	2862.4
tpwr	53	rp	170.5
pw	6.450	lp	13.6
DECOUPLER		is	500
dn		PLOT	
dof	0	wc	250
dm	nnn	sc	0
dmm	c	vs	91
dpwr	33	th	6
dmf	29412	ai ph	

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM
1	2862.406	7.160	207.1	40	1747.554	4.371	16.4	79	620.616	1.552
2	2670.392	6.680	7.5	41	1620.455	4.053	7.1	80	517.104	1.293
3	2662.984	6.661	14.8	42	1619.090	4.050	14.7	81	444.782	1.113
4	2655.576	6.643	7.6	43	1613.437	4.036	22.5	82	396.048	0.991
5	2495.142	6.241	17.7	44	1611.877	4.032	47.1	83	394.683	0.987
6	2487.930	6.223	18.0	45	1606.224	4.018	23.1	84	393.513	0.984
7	2487.345	6.222	8.9	46	1604.859	4.014	49.1	85	392.344	0.981
8	2485.395	6.217	18.9	47	1599.206	4.000	7.8	86	391.369	0.979
9	2480.132	6.204	7.9	48	1597.647	3.996	15.8	87	389.030	0.973
10	2478.183	6.199	20.5	49	1175.995	2.942	65.8	88	387.665	0.970
11	2477.598	6.197	9.5	50	1080.086	2.702	160.8	89	381.817	0.955
12	2470.385	6.179	7.7	51	1016.926	2.544	7.9	90	380.453	0.952
13	2298.060	5.748	8.6	52	1013.807	2.536	9.0			
14	2291.237	5.731	8.9	53	1005.035	2.514	7.2			
15	2280.905	5.705	6.7	54	943.239	2.359	12.4			
16	2272.328	5.684	18.5	55	937.976	2.346	9.3			
17	2271.743	5.683	19.2	56	935.052	2.339	9.5			
18	2262.581	5.660	17.6	57	931.543	2.330	10.0			
19	2261.996	5.658	16.5	58	925.500	2.315	9.5			
20	2224.958	5.565	7.3	59	918.092	2.297	8.6			
21	2224.373	5.564	7.5	60	905.421	2.265	10.8			
22	2215.211	5.541	7.0	61	896.454	2.242	10.0			
23	2214.626	5.540	6.6	62	888.656	2.223	24.8			
24	2013.645	5.037	10.9	63	882.029	2.206	14.9			
25	2011.696	5.032	12.3	64	880.859	2.203	15.0			
26	2010.136	5.028	7.3	65	879.689	2.200	23.2			
27	1996.490	4.994	9.7	66	874.426	2.187	14.1			
28	1994.541	4.989	10.7	67	873.256	2.184	13.5			
29	1993.176	4.986	6.8	68	866.434	2.167	6.9			
30	1985.574	4.967	6.8	69	858.246	2.147	7.8			
31	1984.404	4.964	13.1	70	853.373	2.135	20.7			
32	1983.624	4.962	10.6	71	841.676	2.105	16.9			
33	1982.455	4.959	11.2	72	836.608	2.093	12.3			
34	1974.267	4.938	12.2	73	824.912	2.063	10.1			
35	1973.488	4.936	9.9	74	649.662	1.625	7.3			
36	1972.318	4.934	10.7	75	643.619	1.610	8.3			
37	1785.177	4.465	6.7	76	641.085	1.604	14.0			
38	1778.160	4.448	6.6	77	633.287	1.584	17.1			
39	1754.572	4.389	16.8	78	625.880	1.566	7.8			



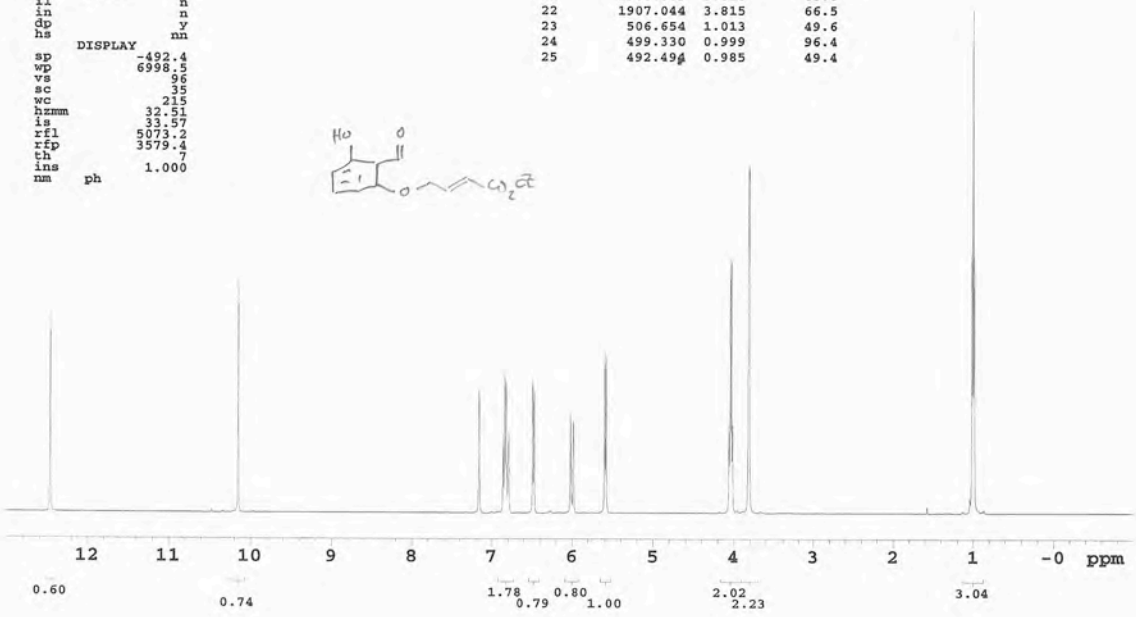

JGMM-Char-R2_CO2Et_spiroC
expl s2pul
SAMPLE
date Feb 27 2008
solvent Benzene
file /data/jasonm/~
JasonMCharacteriza~
tion/JGMM-Char-R2_~
CO2Et_spiroC.fid
ACQUISITION
sfrq 125.716
tn C13
at 1.300
np 97552
sw 37505.9
fb 21000
bs 4
tpwr 53
pw 6.0
d1 1.500
tof 0
nt 3200
ct 420
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1279.5
wp 28415.5
vs 903
sc 0
wc 250
hzmm 113.66
is 500.00
rfl 22891.8
rfp 16090.1
th 8
ins 100.000
nm ph
DEC. & VT
dfrq 499.920
dn H1
dpwr 34
dof 0
dm yyy
dmm w
dmf 10994
dseq
dres 1.0
homo n
PROCESSING
lb 0.50
wtfile
proc ft
fn not used
math f
werr
wexp wft
wbs wft
wnt
INDEX FREQUENCY PPM HEIGHT
1 24603.592 195.726 23.9
2 21942.424 174.556 27.1
3 20992.989 167.003 24.9
4 20701.119 164.681 32.0
5 17994.740 143.151 30.3
6 17683.985 140.679 57.1
7 17666.816 140.543 10.1
8 17349.193 138.016 28.2
9 16701.356 132.862 33.7
10 16126.773 128.291 55.0
11 16114.182 128.191 874.5
12 16103.309 128.105 32.5
13 16090.146 128.000 900.1
14 16078.700 127.909 37.7
15 16065.537 127.804 902.8
16 14901.491 118.544 13.6
17 14894.624 118.489 54.3
18 14498.024 115.334 30.7
19 12014.840 95.580 70.0
20 12002.250 95.480 12.9
21 10760.944 85.605 34.0
22 7597.875 60.442 33.8
23 6992.388 55.626 8.8
24 6935.159 55.170 32.0
25 5981.717 47.586 58.7
26 5762.528 45.842 12.0
27 4300.317 34.210 61.1
28 4240.226 33.732 70.6
29 4232.214 33.668 16.2
30 4018.748 31.970 13.7
31 3790.975 30.158 11.5
32 3656.486 29.088 59.6
33 3606.124 28.687 11.6
34 3421.273 27.217 60.8
35 3389.797 26.966 11.9
36 3354.315 26.684 12.2
37 3349.737 26.648 58.9
38 1791.952 14.255 63.6
OEt
OH
200
180
160
140
120
100
80
60
40
20
ppm

JGMM-XI-Char-Crotylate - Re-purification
of VII-1006 and 970

expl s2pul

SAMPLE		DEC. & VT	
date	May 13 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
	JasonMCharacteriza~	dof	0
	tion/JGMM-Char-Cro~	dm	nnn
	tylate.fid	dmm	c
ACQUISITION		dmf	200
sfrq	499.920	dseq	
tn	H1	dres	1.0
at	1.892	homo	n
np	30272	temp	20.0
sw	8000.0	PROCESSING	
fb	4000	wtfile	
bs	4	proc	ft
tpwr	58	fn	not used
pw	5.5	math	f
d1	2.000		
tof	0	werr	
nt	320	wexp	wft
ct	12	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-492.4		
wp	6998.5		
vs	96		
sc	35		
wc	215		
hzmm	32.51		
is	33.57		
rfl	5073.2		
rfp	3579.4		
th	7		
ins	1.000		
nm	ph		

INDEX	FREQUENCY	PPM	HEIGHT
1	6233.705	12.469	37.9
2	5075.990	10.154	44.8
3	3579.408	7.160	23.5
4	3429.994	6.861	14.9
5	3421.693	6.845	30.0
6	3412.904	6.827	25.1
7	3407.533	6.816	9.5
8	3399.232	6.800	9.3
9	3395.814	6.793	15.3
10	3391.419	6.784	8.7
11	3243.470	6.488	25.6
12	3235.169	6.471	23.1
13	3008.607	6.018	19.0
14	2992.982	5.987	17.5
15	2799.134	5.599	30.7
16	2790.834	5.583	29.8
17	2030.091	4.061	16.9
18	2022.767	4.046	48.4
19	2015.443	4.032	48.2
20	2008.607	4.018	17.9
21	1908.509	3.818	65.8
22	1907.044	3.815	66.5
23	506.654	1.013	49.6
24	499.330	0.999	96.4
25	492.494	0.985	49.4

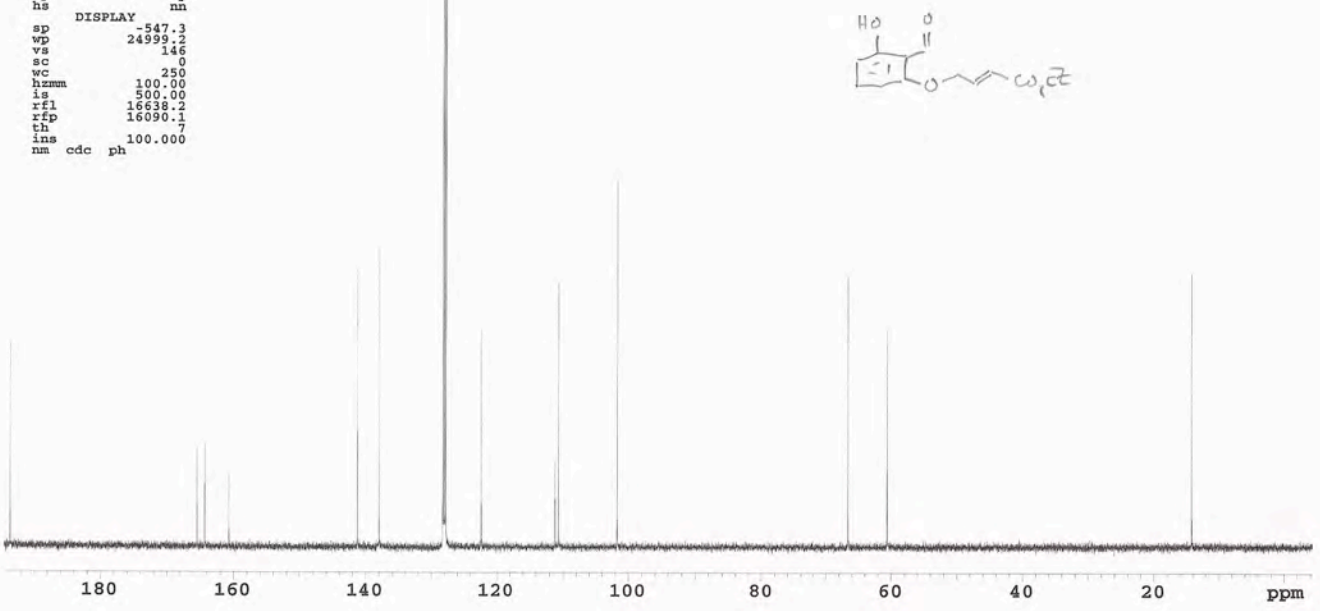


JGMM-Char-Crotylate - Re-purification of VII-1006 and 970

exp2 s2pul

SAMPLE		DEC. & VT	
date	May 13 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	34
	JasonMCharacteriza~	dof	0
	tion/JGMM-Char-Cro~	dm	yyy
	tylateC.fid	dmm	w
ACQUISITION		dmf	10994
sfrq	125.716	dseq	
tn	C13	dres	1.0
at	1.300	homo	n
np	65024	temp	20.0
sw	25000.0	PROCESSING	
fb	14000	lb	0.50
bs	4	wtfile	
tpwr	53	proc	ft
pw	6.0	fn	not used
d1	1.500	math	f
tof	0		
nt	3200	werr	
ct	32	wexp	wft
alock	n	wbs	wft
gain	not used	wnt	
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-547.3		
wp	24999.2		
vs	146		
sc	0		
wc	250		
hzmm	100.00		
is	500.00		
rfl	16638.2		
rfp	16090.1		
th	7		
ins	100.000		
nm cdc ph			

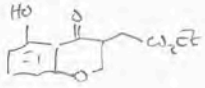
INDEX	FREQUENCY	PPM	HEIGHT
1	24343.625	193.658	39.5
2	20796.719	165.442	18.8
3	20656.338	164.325	19.5
4	20199.338	160.689	13.7
5	17755.643	141.249	53.1
6	17347.470	138.002	57.1
7	16114.560	128.194	142.4
8	16090.146	128.000	145.9
9	16065.732	127.806	143.7
10	15384.427	122.386	41.7
11	13976.804	111.188	16.3
12	13914.243	110.690	50.4
13	12784.329	101.702	70.0
14	8375.302	66.627	51.7
15	7613.126	60.564	41.6
16	1783.505	14.188	52.2



JGMM-Char-Stetter - Re-purification of V II-1010a and 1089a

expl s2pul

SAMPLE		DEC. & VT	
date	May 13 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
	JasonMCharacteriza~	dof	0
	tion/JGMM-Char-Ste~	dm	nnn
	tter.fid	dmm	c
ACQUISITION		dmf	200
sfrq	499.920	dseq	
tn	H1	dres	1.0
at	1.892	homo	n
np	30272	temp	20.0
sw	8000.0	PROCESSING	
fb	4000	wtfile	
bs	4	proc	ft
tpwr	58	fn	not used
pw	5.5	math	f
dl	2.000		
tof	0	werr	
nt	320	wexp	wft
ct	8	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-491.9		
wp	6998.5		
vs	216		
sc	35		
wc	215		
hzmm	32.51		
is	33.57		
rfl	5072.8		
rfp	3579.4		
th	4		
ins	1.000		
nm	ph		



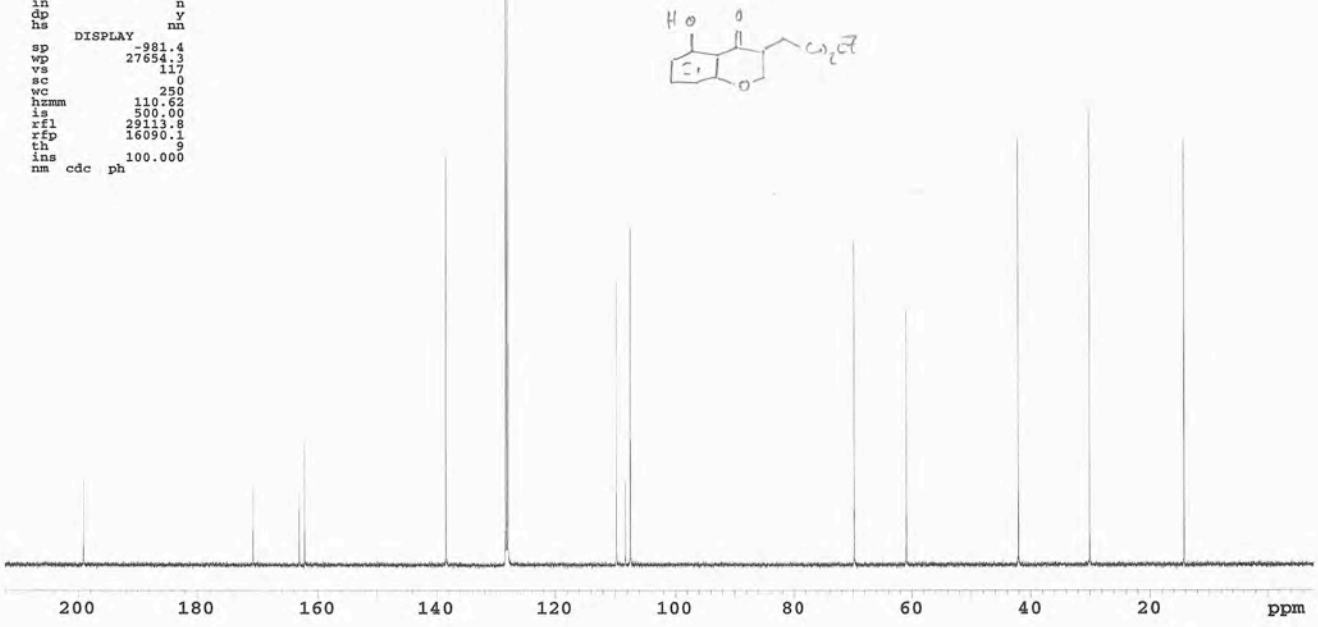
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	6060.853	12.124	56.9	40	945.130	1.891	14.7
2	3579.408	7.160	216.0	41	937.318	1.875	14.3
3	3446.595	6.894	13.5	42	455.873	0.912	56.8
4	3438.294	6.878	28.5	43	448.548	0.897	106.5
5	3429.994	6.861	15.6	44	442.201	0.885	49.4
6	3250.306	6.502	21.9	45	212.709	0.425	10.2
7	3242.005	6.485	20.0				
8	3141.419	6.284	26.4				
9	3140.443	6.282	19.6				
10	3133.119	6.267	24.8				
11	3132.142	6.265	17.1				
12	1962.709	3.926	14.0				
13	1956.849	3.914	15.3				
14	1951.478	3.904	19.5				
15	1949.525	3.900	6.9				
16	1946.107	3.893	24.8				
17	1942.201	3.885	6.2				
18	1938.783	3.878	21.0				
19	1932.435	3.866	27.3				
20	1925.599	3.852	23.0				
21	1922.181	3.845	5.7				
22	1918.763	3.838	7.0				
23	1914.857	3.830	5.0				
24	1824.037	3.649	16.1				
25	1812.806	3.626	26.7				
26	1801.087	3.603	14.4				
27	1439.271	2.879	6.4				
28	1433.412	2.867	5.3				
29	1431.947	2.864	8.9				
30	1427.064	2.855	8.9				
31	1424.134	2.849	5.2				
32	1421.693	2.844	4.7				
33	1419.252	2.839	6.9				
34	1231.263	2.463	15.7				
35	1226.380	2.453	15.1				
36	1214.173	2.429	17.8				
37	1209.291	2.419	16.9				
38	962.220	1.925	16.4				
39	954.408	1.909	16.1				

JGMM-Char-StetterC - Re-purification of VII-1010a and 1089a

exp2 s2pul

SAMPLE		DEC. & VT	
date	May 13 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/-	dpwr	34
	JasonMCharacteriza-	dof	0
	tion/JGMM-Char-Ste-	dm	yyy
	tterC.fid	dmm	w
ACQUISITION		dmf	10994
sfrq	125.716	dseq	
tn	C13	dres	1.0
at	1.300	homo	n
np	130048	temp	20.0
sw	50000.0	PROCESSING	
fb	28000	lb	0.50
bs	4	wtfile	
tpwr	53	proc	ft
pw	6.0	fn	not used
d1	1.500	math	f
tof	0		
nt	3200	werr	
ct	40	wexp	wft
alock	n	wbs	wft
gain	not used	wnt	
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-981.4		
wp	27654.3		
vs	117		
sc	0		
wc	250		
hzmm	110.62		
is	500.00		
rfl	29113.8		
rfp	16090.1		
th	9		
ins	100.000		
nm	cdc ph		

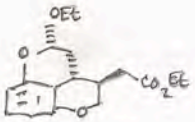
INDEX	FREQUENCY	PPM	HEIGHT
1	25026.453	199.090	17.4
2	21469.629	170.795	15.3
3	20510.614	163.166	13.6
4	20395.410	162.249	23.3
5	17403.924	138.451	77.8
6	16138.971	128.388	112.3
7	16114.557	128.194	117.4
8	16090.143	128.000	116.6
9	13798.273	109.768	53.8
10	13617.456	108.329	15.6
11	13506.067	107.443	64.2
12	8766.687	69.741	61.6
13	7659.662	60.934	48.5
14	5283.868	42.034	81.0
15	3771.722	30.005	86.8
16	1791.131	14.249	81.0



JGMM-Char-XI-1599 - Isocyanate/EVE [4+2]
w/ reduced chromanone

expl s2pul

SAMPLE		SPECIAL	
date	May 18 2007	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/~	spin	20
	JasonMCharacteriza~	hst	0.008
	tion/JGMM-Char-XI-~	pw90	11.500
	1599.fid	alfa	-6.900
ACQUISITION		FLAGS	
sw	4789.3	il	n
at	3.000	in	n
np	28736	dp	y
fb	not used	hs	nn
bs	2	PROCESSING	
ss	2	lb	0.30
d1	1.000	fn	65536
nt	32	DISPLAY	
ct	8	sp	-149.9
TRANSMITTER		wp	2997.5
tn	H1	rf1	2729.3
sfrq	299.763	rfp	2146.3
tof	265.1	rp	159.3
tpwr	58	lp	-7.1
pw	5.600	PLOT	
DECOUPLER		wc	250
dn	C13	sc	0
dof	0	vs	391
dm	nnn	th	8
dmm	c	ai	ph
dpwr	46		
dmf	13100		



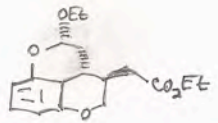
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2146.353	7.160	92.2	40	589.781	1.968	9.5
2	2091.983	6.979	11.7	41	587.589	1.960	17.7
3	2083.944	6.952	26.1	42	583.204	1.946	26.3
4	2075.759	6.925	15.9	43	577.212	1.926	11.2
5	1993.327	6.650	27.8	44	573.119	1.912	14.1
6	1989.526	6.637	25.1	45	569.758	1.901	11.2
7	1988.796	6.635	24.4	46	568.588	1.897	10.6
8	1985.288	6.623	24.1	47	556.603	1.857	7.9
9	1981.342	6.610	20.5	48	500.041	1.668	16.9
10	1980.611	6.607	20.7	49	492.148	1.642	14.8
11	1483.531	4.949	15.0	50	484.694	1.617	13.9
12	1480.462	4.939	16.9	51	476.948	1.591	11.7
13	1474.031	4.917	16.6	52	424.478	1.416	8.5
14	1470.962	4.907	17.3	53	414.831	1.384	9.1
15	1269.557	4.235	14.5	54	411.762	1.374	15.6
16	1266.049	4.224	15.7	55	402.262	1.342	14.8
17	1258.888	4.200	16.3	56	399.192	1.332	8.2
18	1255.380	4.188	17.0	57	352.276	1.175	53.1
19	1213.725	4.049	13.0	58	345.260	1.152	107.4
20	1206.710	4.026	13.8	59	338.245	1.128	51.8
21	1204.371	4.018	16.0	60	273.497	0.912	50.0
22	1197.356	3.994	14.9	61	266.336	0.888	98.9
23	1162.132	3.877	15.6	62	259.174	0.865	48.8
24	1154.970	3.853	47.4	63	257.128	0.858	18.2
25	1147.808	3.829	48.6	64	168.118	0.561	9.5
26	1140.647	3.805	17.0				
27	1073.268	3.580	15.5				
28	1062.453	3.544	29.2				
29	1051.637	3.508	15.2				
30	1034.391	3.451	13.3				
31	1027.375	3.427	14.5				
32	1025.037	3.420	13.8				
33	1018.021	3.396	12.6				
34	656.867	2.191	8.2				
35	654.382	2.183	9.4				
36	645.759	2.154	9.1				
37	641.959	2.142	9.0				
38	603.227	2.012	11.7				
39	598.697	1.997	14.1				

JGMM-Char-XI-1599C - Carbon of isocyanate/EVE [4+2] w/ reduced chromanone

expl s2pul

SAMPLE		SPECIAL	
date	May 18 2007	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/~	spin	20
	JasonMCharacteriza~	hst	0.008
	tion/JGMM-Char-XI-~	pw90	17.100
	1599C.fid	alfa	-8.800
ACQUISITION		FLAGS	
sw	18797.0	il	n
at	2.500	in	n
np	93984	dp	y
fb	not used	hs	nn
bs	4	PROCESSING	
dl	1.000	lb	1.00
nt	3200	fn	131072
ct	504	DISPLAY	
TRANSMITTER		sp	135.1
tn	C13	wp	13588.4
sfrq	75.383	rfl	10772.4
tof	727.6	rfp	9648.0
tpwr	60	rp	139.4
pw	6.000	lp	4.3
DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	707
dmm	w	th	10
dpwr	40	ai	ph
dmf	11900		

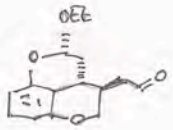
INDEX	FREQUENCY	PPM	HEIGHT
1	12853.494	170.527	26.7
2	11609.272	154.020	21.0
3	11598.947	153.883	22.0
4	9697.621	128.658	41.3
5	9648.001	128.000	728.7
6	9623.622	127.677	727.7
7	9599.529	127.357	722.5
8	8175.184	108.460	21.2
9	8157.401	108.224	41.9
10	8141.626	108.015	41.3
11	7535.864	99.978	37.8
12	5219.798	69.251	36.3
13	4808.499	63.794	37.4
14	4529.137	60.088	37.6
15	2554.959	33.897	43.2
16	2515.378	33.372	44.0
17	2476.657	32.858	46.5
18	2401.224	31.857	34.5
19	1137.785	15.095	40.7
20	1038.832	13.782	35.0



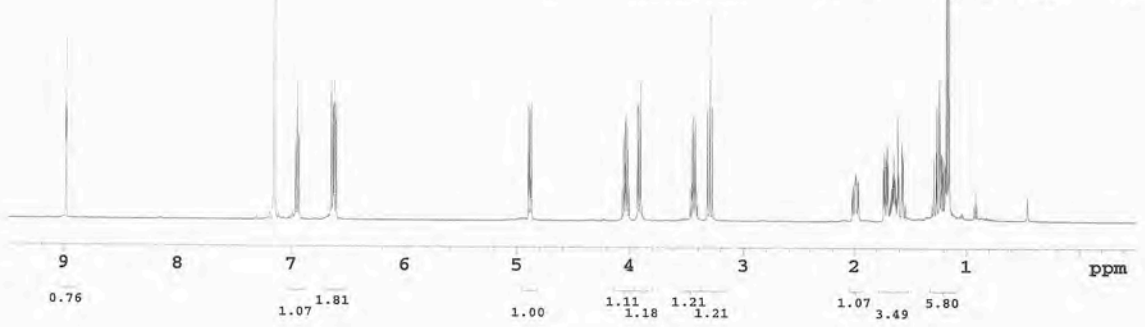
JGMM-Char-R2ald

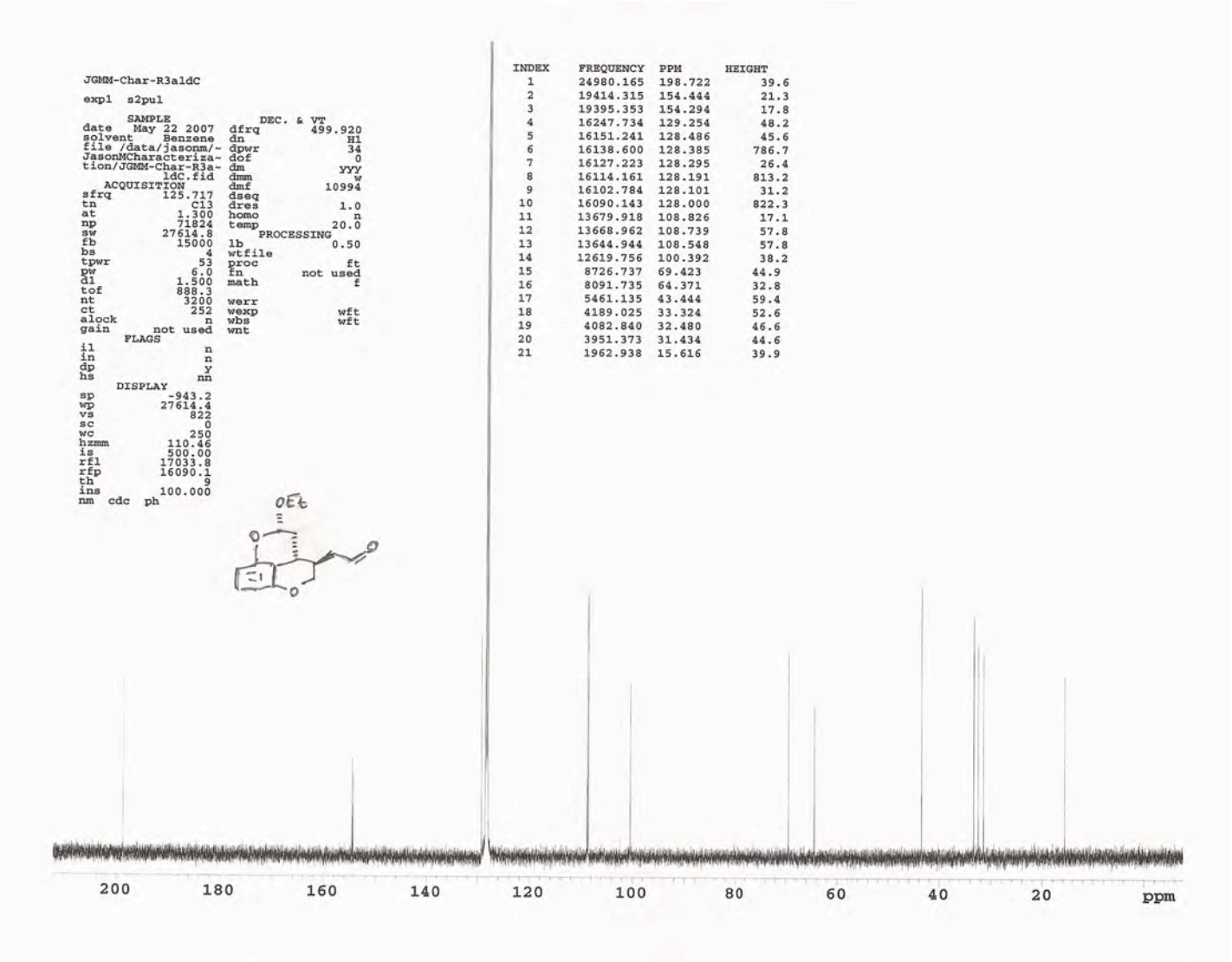
expl s2pul

SAMPLE		DEC. & VT	
date	May 22 2007	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
	JasonMCharacteriza~	dof	0
	tion/JGMM-Char-S3a~	dm	nnn
	1d.fid	dmm	c
ACQUISITION		dmf	200
sfrq	499.920	dseq	
tn	H1	dres	1.0
at	1.892	homo	n
np	30272	temp	20.0
sw	8000.0	PROCESSING	
fb	4000	wtfile	
bs	4	proc	ft
tpwr	58	fn	not used
pw	5.5	math	f
d1	2.000		
tof	0	werr	
nt	320	wexp	wft
ct	16	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	151		
sc	35		
wc	215		
hzmm	23.22		
is	33.57		
rfl	5072.3		
rfp	3579.4		
th	7		
ins	1.000		
nm	ph		



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM
1	4492.494	8.986	21.8	40	997.376	1.995	8.5	79	583.802	1.168
2	4491.029	8.984	34.8	41	995.423	1.991	9.3	80	576.478	1.153
3	4489.076	8.980	21.0	42	993.470	1.987	8.6			
4	3579.408	7.160	146.9	43	986.634	1.974	7.6			
5	3485.169	6.971	14.8	44	982.728	1.966	8.0			
6	3484.193	6.970	13.1	45	870.423	1.741	10.0			
7	3476.869	6.955	32.3	46	867.005	1.734	13.3			
8	3468.568	6.938	16.2	47	866.029	1.732	12.6			
9	3325.990	6.653	24.4	48	862.611	1.726	10.8			
10	3325.013	6.651	27.3	49	857.728	1.716	12.3			
11	3317.689	6.636	21.8	50	854.310	1.709	14.7			
12	3316.712	6.635	22.2	51	853.334	1.707	14.2			
13	3313.294	6.628	27.1	52	850.404	1.701	11.2			
14	3312.318	6.626	22.4	53	828.919	1.658	8.6			
15	3304.994	6.611	22.4	54	825.501	1.651	9.3			
16	3304.017	6.609	18.5	55	823.548	1.647	12.7			
17	2449.037	4.899	21.9	56	821.107	1.642	8.2			
18	2446.107	4.893	21.4	57	817.689	1.636	8.4			
19	2439.271	4.879	21.5	58	806.947	1.614	20.2			
20	2436.341	4.873	22.8	59	805.482	1.611	16.8			
21	2026.673	4.054	16.5	60	802.552	1.605	8.8			
22	2024.720	4.050	7.1	61	801.087	1.602	9.4			
23	2019.837	4.040	19.1	62	789.857	1.580	14.7			
24	2017.396	4.035	20.4	63	788.392	1.577	15.4			
25	2010.560	4.022	18.1	64	784.974	1.570	12.6			
26	1966.126	3.933	22.2	65	783.998	1.568	12.2			
27	1962.709	3.926	22.3	66	643.861	1.288	12.7			
28	1955.384	3.911	22.5	67	634.584	1.269	13.4			
29	1951.966	3.905	26.5	68	631.166	1.263	22.1			
30	1726.380	3.453	18.9	69	621.888	1.244	27.1			
31	1723.939	3.448	7.4	70	618.959	1.238	21.2			
32	1719.056	3.439	20.0	71	613.099	1.226	12.9			
33	1717.103	3.435	17.1	72	611.634	1.223	12.9			
34	1712.220	3.425	7.4	73	609.193	1.219	12.4			
35	1709.779	3.420	19.3	74	603.822	1.208	12.4			
36	1658.998	3.319	21.5	75	601.869	1.204	12.0			
37	1648.255	3.297	40.0	76	596.009	1.192	10.6			
38	1637.513	3.276	22.0	77	594.056	1.188	11.0			
39	999.330	1.999	7.6	78	590.638	1.181	72.2			




JGMM-Char-R3aldC
expl s2pul
SAMPLE
date May 22 2007
solvent Benzene
file /data/jasonm/~
JasonMCharacteriza~
tion/JGMM-Char-R3a~
1dc.fid
ACQUISITION
sfrq 125.717
tn C13
at 1.300
np 71824
sw 27614.8
fb 15000
bs 4
tpwr 53
pw 6.0
dl 1.500
tof 888.3
nt 3200
ct 252
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -943.2
wp 27614.4
vs 822
sc 0
wc 250
hzmm 110.46
is 500.00
rfl 17033.8
rfp 16090.1
th 9
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.920
dn H1
dpwr 34
dof 0
dm yyy
dmm w
dmf 10994
dseq
dres 1.0
homo n
temp 20.0
PROCESSING
lb 0.50
wtfile
proc ft
fn not used
math f
werr
wexp wft
wbs wft
wnt
OEt
O
O
O
INDEX FREQUENCY PPM HEIGHT
1 24980.165 198.722 39.6
2 19414.315 154.444 21.3
3 19395.353 154.294 17.8
4 16247.734 129.254 48.2
5 16151.241 128.486 45.6
6 16138.600 128.385 786.7
7 16127.223 128.295 26.4
8 16114.161 128.191 813.2
9 16102.784 128.101 31.2
10 16090.143 128.000 822.3
11 13679.918 108.826 17.1
12 13668.962 108.739 57.8
13 13644.944 108.548 57.8
14 12619.756 100.392 38.2
15 8726.737 69.423 44.9
16 8091.735 64.371 32.8
17 5461.135 43.444 59.4
18 4189.025 33.324 52.6
19 4082.840 32.480 46.6
20 3951.373 31.434 44.6
21 1962.938 15.616 39.9
200
180
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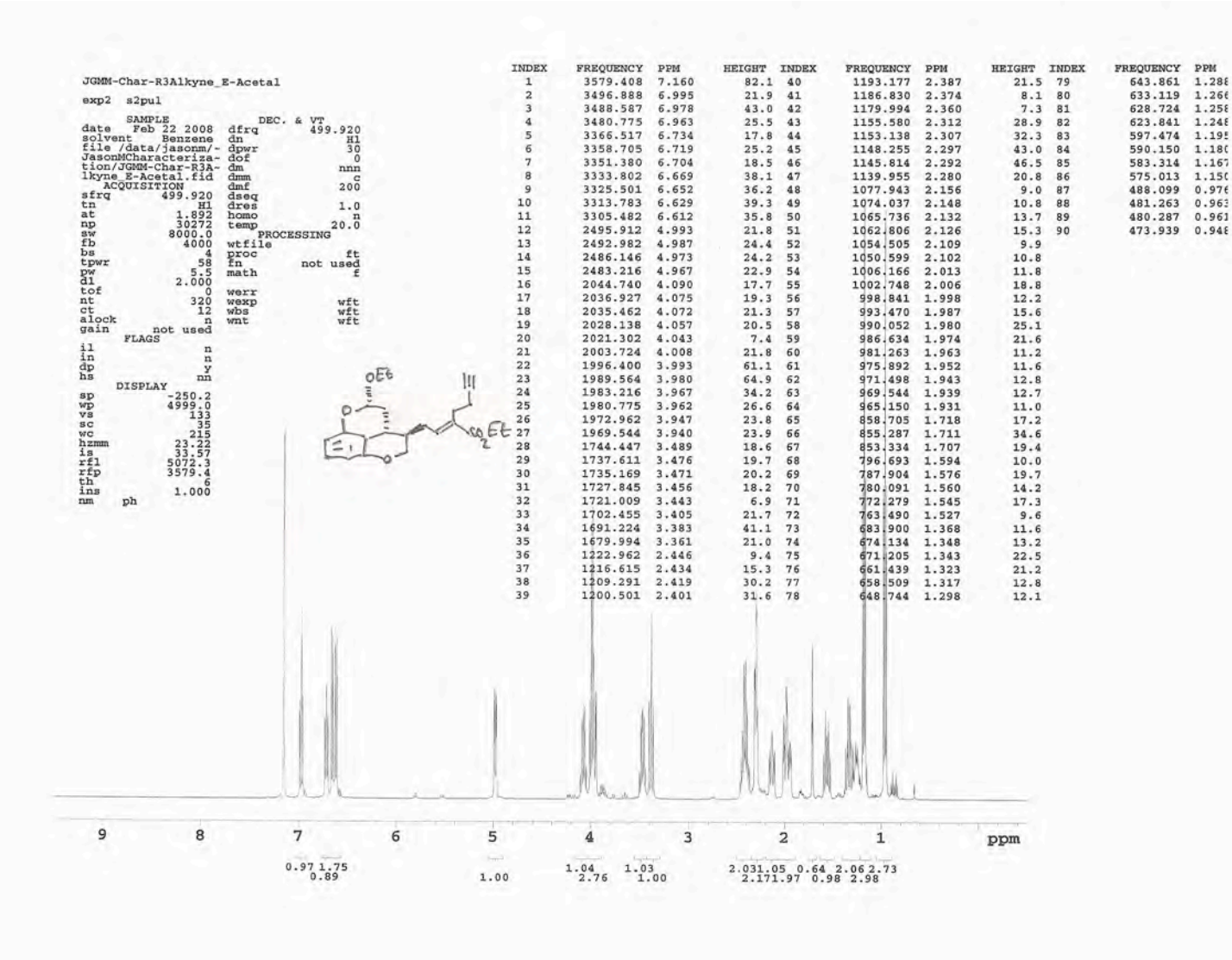


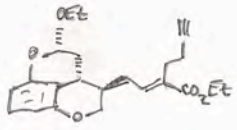
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM
1	3579.408	7.160	82.1	40	1193.177	2.387	21.5	79	643.861	1.286
2	3496.888	6.995	21.9	41	1186.830	2.374	8.1	80	633.119	1.266
3	3488.587	6.978	43.0	42	1179.994	2.360	7.3	81	628.724	1.258
4	3480.775	6.963	25.5	43	1155.580	2.312	28.9	82	623.841	1.248
5	3366.517	6.734	17.8	44	1153.138	2.307	32.3	83	597.474	1.195
6	3358.705	6.719	25.2	45	1148.255	2.297	43.0	84	590.150	1.180
7	3351.380	6.704	18.5	46	1145.814	2.292	46.5	85	583.314	1.167
8	3333.802	6.669	38.1	47	1139.955	2.280	20.8	86	575.013	1.150
9	3325.501	6.652	36.2	48	1077.943	2.156	9.0	87	488.099	0.976
10	3313.783	6.629	39.3	49	1074.037	2.148	10.8	88	481.263	0.963
11	3305.482	6.612	35.8	50	1065.736	2.132	13.7	89	480.287	0.961
12	2495.912	4.993	21.8	51	1062.806	2.126	15.3	90	473.939	0.948
13	2492.982	4.987	24.4	52	1054.505	2.109	9.9			
14	2486.146	4.973	24.2	53	1050.599	2.102	10.8			
15	2483.216	4.967	22.9	54	1006.166	2.013	11.8			
16	2044.740	4.090	17.7	55	1002.748	2.006	18.8			
17	2036.927	4.075	19.3	56	998.841	1.998	12.2			
18	2035.462	4.072	21.3	57	993.470	1.987	15.6			
19	2028.138	4.057	20.5	58	990.052	1.980	25.1			
20	2021.302	4.043	7.4	59	986.634	1.974	21.6			
21	2003.724	4.008	21.8	60	981.263	1.963	11.2			
22	1996.400	3.993	61.1	61	975.892	1.952	11.6			
23	1989.564	3.980	64.9	62	971.498	1.943	12.8			
24	1983.216	3.967	34.2	63	969.544	1.939	12.7			
25	1980.775	3.962	26.6	64	965.150	1.931	11.0			
26	1972.962	3.947	23.8	65	858.705	1.718	17.2			
27	1969.544	3.940	23.9	66	855.287	1.711	34.6			
28	1744.447	3.489	18.6	67	853.334	1.707	19.4			
29	1737.611	3.476	19.7	68	796.693	1.594	10.0			
30	1735.169	3.471	20.2	69	787.904	1.576	19.7			
31	1727.845	3.456	18.2	70	780.091	1.560	14.2			
32	1721.009	3.443	6.9	71	772.279	1.545	17.3			
33	1702.455	3.405	21.7	72	763.490	1.527	9.6			
34	1691.224	3.383	41.1	73	683.900	1.368	11.6			
35	1679.994	3.361	21.0	74	674.134	1.348	13.2			
36	1222.962	2.446	9.4	75	671.205	1.343	22.5			
37	1216.615	2.434	15.3	76	661.439	1.323	21.2			
38	1209.291	2.419	30.2	77	658.509	1.317	12.8			
39	1200.501	2.401	31.6	78	648.744	1.298	12.1			

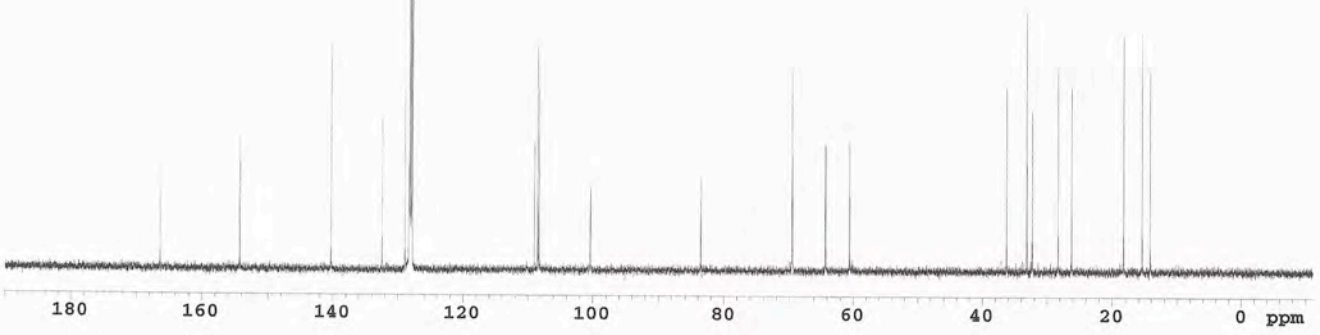
JGMM-Char-R3Alkyne_E-AcetalC

exp1 s2pul

SAMPLE		DEC. & VT	
date	Feb 22 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	34
	JasonMCharacteriza~	dof	0
	tion/JGMM-Char-R3A~	dm	yyy
	lkyne_E-AcetalC.fi~	dmm	w
	d	dmf	10994
ACQUISITION		dseq	
sfrq	125.716	dres	1.0
tn	C13	homo	n
at	1.300	temp	20.0
np	130048	PROCESSING	
sw	50000.0	lb	0.50
fb	28000	wtfile	
bs	4	proc	ft
tpwr	53	fn	not used
pw	6.0	math	f
dl	1.500		
tof	0	werr	
nt	1000	wexp	wft
ct	120	wbs	wft
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1385.7		
wp	25267.8		
vs	282		
sc	0		
wc	250		
hzmm	101.07		
is	500.00		
rfl	29138.9		
rfp	16090.1		
th	11		
ins	100.000		
nm cdc ph			

INDEX	FREQUENCY	PPM	HEIGHT
1	20910.397	166.346	19.8
2	19400.540	154.335	24.6
3	19389.096	154.244	20.2
4	17641.965	140.345	42.8
5	16650.143	132.455	28.8
6	16207.639	128.935	34.6
7	16126.767	128.291	19.6
8	16114.560	128.194	262.3
9	16090.146	128.000	278.3
10	16065.732	127.806	282.0
11	13699.094	108.979	24.1
12	13638.059	108.493	42.6
13	13614.407	108.305	34.5
14	12613.431	100.342	15.5
15	10502.377	83.548	17.3
16	8745.328	69.571	38.2
17	8738.461	69.516	21.8
18	8075.467	64.242	24.0
19	7609.311	60.533	24.3
20	4559.079	36.268	35.0
21	4162.351	33.112	49.3
22	4062.405	32.317	30.5
23	3555.051	28.281	38.5
24	3294.125	26.205	35.0
25	2298.489	18.285	44.9
26	1942.197	15.451	45.5
27	1785.031	14.200	38.1

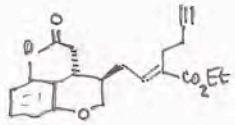




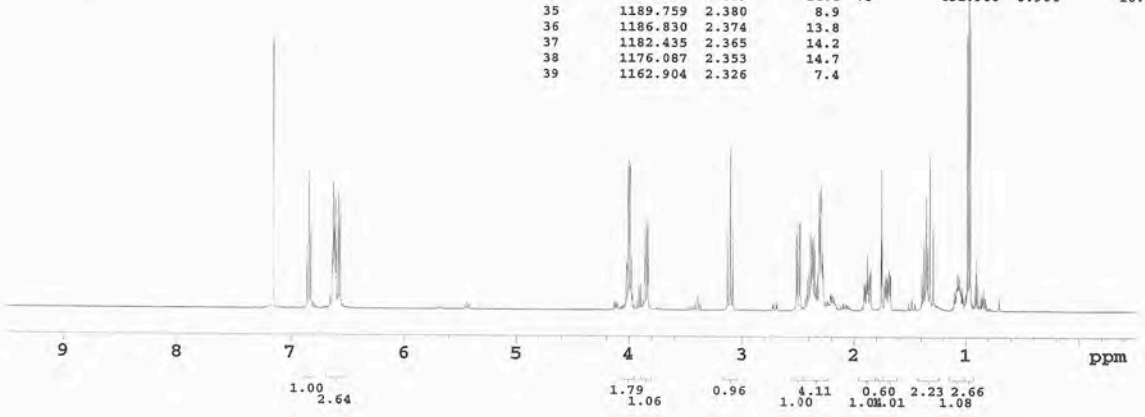
JGMM-Char-R3Alkyne_E-Lactone

exp2 s2pul

SAMPLE		DEC. & VT	
date	Feb 22 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
	JasonMCharacteriza~	dof	0
	tion/JGMM-Char-R3A~	dm	nnn
	lkyne_E-Lactone.fi~	dmm	c
	d	dmf	200
ACQUISITION		dseq	
sfrq	499.920	dres	1.0
tn	H1	homo	n
at	1.892	temp	20.0
np	30272	PROCESSING	
sw	8000.0	wtfile	
fb	4000	proc	ft
bs	2	fn	not used
tpwr	58	math	f
pw	5.5		
dl	2.000	werr	
tof	0	wexp	wft
nt	320	wbs	wft
ct	12	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	115		
sc	35		
wc	215		
hzmm	23.22		
is	1434.49		
rf1	5072.3		
rfp	3579.4		
th	6		
ins	1.000		
nm	ph		



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3579.408	7.160	51.4	40	1155.580	2.312	22.2
2	3428.041	6.857	12.5	41	1153.138	2.307	23.3
3	3419.740	6.841	27.3	42	1148.255	2.297	23.6
4	3411.439	6.824	15.7	43	1145.814	2.292	24.4
5	3316.712	6.635	12.6	44	1142.396	2.285	9.5
6	3313.294	6.628	24.6	45	1139.955	2.280	11.3
7	3310.365	6.622	15.7	46	1138.001	2.276	7.8
8	3307.923	6.617	15.7	47	940.736	1.882	10.8
9	3304.994	6.611	21.3	48	936.830	1.874	6.3
10	3301.576	6.604	13.8	49	930.482	1.861	7.1
11	3292.298	6.586	23.4	50	926.087	1.852	8.3
12	3284.486	6.570	20.5	51	880.189	1.761	13.8
13	2012.025	4.025	9.0	52	877.748	1.756	27.2
14	2010.560	4.022	9.3	53	875.306	1.751	13.4
15	2004.701	4.010	27.5	54	859.681	1.720	6.7
16	2003.236	4.007	28.7	55	857.728	1.716	6.8
17	1997.865	3.996	27.4	56	853.822	1.708	6.5
18	1995.912	3.992	28.1	57	848.451	1.697	7.1
19	1990.541	3.982	10.5	58	844.056	1.688	7.9
20	1989.076	3.979	9.8	59	842.103	1.684	7.8
21	1930.482	3.862	16.0	60	838.197	1.677	6.9
22	1927.064	3.855	17.0	61	696.595	1.393	7.3
23	1919.740	3.840	17.1	62	687.806	1.376	13.8
24	1915.834	3.832	16.5	63	680.970	1.362	7.9
25	1565.736	3.132	16.2	64	677.552	1.355	22.1
26	1554.505	3.110	31.2	65	672.181	1.345	12.1
27	1543.275	3.087	15.4	66	662.904	1.326	29.5
28	1259.095	2.519	16.2	67	648.255	1.297	16.2
29	1254.701	2.510	17.0	68	537.416	1.075	7.3
30	1243.959	2.488	16.6	69	527.650	1.055	6.8
31	1239.076	2.479	17.4	70	494.935	0.990	52.9
32	1207.337	2.415	6.1	71	487.611	0.975	115.0
33	1201.478	2.403	7.9	72	480.287	0.961	54.4
34	1194.154	2.389	14.4	73	451.966	0.904	10.3
35	1189.759	2.380	8.9				
36	1186.830	2.374	13.8				
37	1182.435	2.365	14.2				
38	1176.087	2.353	14.7				
39	1162.904	2.326	7.4				



JGMM-Char-R3Alkyne_E-LactoneC

exp1 s2pul

SAMPLE		DEC. & VT	
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file	/data/jasonm/~	dpwr	34
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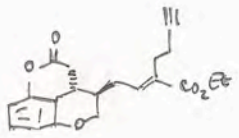
	tion/JGMM-Char-R3A~	dm	yyy
	lkyne_E-LactoneC.f~	dmm	w
	id	dmf	10994
ACQUISITION		dseq	
sfrq	125.716	dres	1.0
tn	C13	homo	n
at	1.300	temp	20.0
np	65024	**PROCESSING**	
sw	25000.0	lb	0.50
fb	14000	wtfile	
bs	4	proc	ft
tpwr	53	fn	not used
pw	6.0	math	f
d1	1.500		
tof	0	werr	
nt	1000	wexp	wft
ct	92	wbs	wft
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-548.0		
wp	24999.2		
vs	372		
sc	0		
wc	250		
hzmm	100.00		
is	500.00		
rfl	16638.9		
rfp	16090.1		
th	12		
ins	100.000		
nm cdc ph			

INDEX	FREQUENCY	PPM	HEIGHT
1	20920.316	166.425	22.9
2	20899.716	166.261	18.5
3	19355.527	153.977	19.1
4	19160.977	152.429	24.8
5	17558.804	139.683	37.4
6	16701.260	132.862	26.4
7	16244.260	129.226	42.0
8	16127.530	128.297	21.5
9	16114.560	128.194	356.8
10	16090.146	128.000	360.6
11	16078.702	127.909	16.2
12	16066.495	127.812	371.7
13	14087.430	112.068	52.7
14	13709.012	109.058	26.4
15	13634.244	108.463	43.1
16	10485.593	83.415	27.0
17	8765.927	69.735	42.2
18	8673.611	69.000	31.4
19	7625.333	60.661	26.0
20	4569.760	36.353	45.4
21	4136.411	32.906	40.4
22	3989.926	31.741	41.5
23	3520.718	28.008	49.0
24	3288.785	26.163	36.5
25	2296.201	18.267	45.7
26	1785.031	14.200	41.3



JGMM-XIV-2011 - R3 alkyne DA

expl PROTON

SAMPLE		DEC. & VT	
date	Feb 22 2008	dfrq	599.776
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
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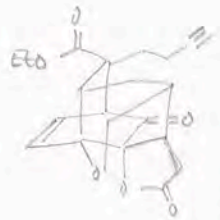
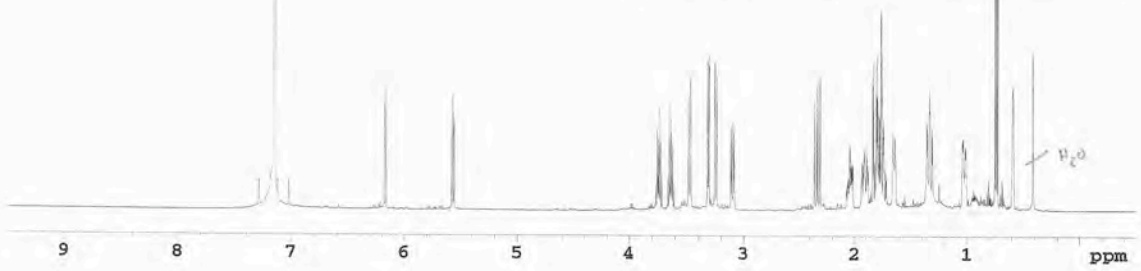
	tion/JGMM-Char-XIV~	dm	nnn
	-2011.fid	dmm	c
ACQUISITION		dmf	200
sfrq	599.776	dseq	
tn	H1	dres	1.0
at	1.892	homo	n
np	30272	temp	25.0
sw	8000.0	PROCESSING	
fb	not used	wtfile	
bs	2	proc	ft
tpwr	59	fn	not used
pw	5.5	math	f
dl	0		
tof	0	werr	
nt	3200	wexp	wft
ct	136	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-300.4		
wp	5997.6		
vs	738		
sc	35		
wc	215		
hzmm	27.86		
is	33.57		
rfl	5266.1		
rfp	4294.4		
th	7		
ins	1.000		
nm	ph		



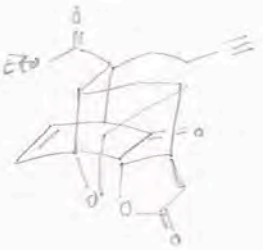
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM
1	4313.907	7.193	7.3	40	1213.810	2.024	9.3	79	627.872	1.047
2	4294.376	7.160	738.2	41	1210.392	2.018	8.5	80	624.943	1.042
3	3705.509	6.178	22.7	42	1207.950	2.014	8.7	81	622.501	1.038
4	3697.208	6.164	23.6	43	1160.099	1.934	7.6	82	620.060	1.034
5	3345.646	5.578	21.4	44	1158.634	1.932	9.1	83	617.130	1.029
6	3339.298	5.568	22.2	45	1155.704	1.927	8.8	84	614.200	1.024
7	3338.322	5.566	15.8	46	1152.286	1.921	8.5	85	611.271	1.019
8	3337.345	5.564	18.6	47	1149.357	1.916	9.9	86	608.829	1.015
9	3330.997	5.554	17.3	48	1147.404	1.913	11.5	87	605.900	1.010
10	2252.872	3.756	15.4	49	1146.427	1.911	11.0	88	450.626	0.751
11	2249.454	3.751	7.1	50	1144.962	1.909	12.1	89	443.790	0.740
12	2246.036	3.745	13.5	51	1135.197	1.893	12.8	90	436.466	0.728
13	2242.130	3.738	19.8	52	1132.755	1.889	9.4	91	355.900	0.593
14	2234.806	3.726	16.9	53	1130.802	1.885	8.3	92	353.458	0.589
15	2227.970	3.715	7.1	54	1127.872	1.880	7.6	93	248.966	0.415
16	2188.907	3.650	20.8	55	1103.458	1.840	25.7			
17	2181.583	3.637	17.6	56	1099.064	1.832	28.1			
18	2178.165	3.632	14.9	57	1091.251	1.819	9.4			
19	2174.747	3.626	7.1	58	1084.904	1.809	27.9			
20	2170.841	3.619	12.4	59	1080.509	1.802	29.5			
21	2091.251	3.487	21.8	60	1077.579	1.797	21.7			
22	2080.997	3.470	25.4	61	1074.650	1.792	9.2			
23	1992.130	3.321	28.6	62	1071.720	1.787	18.2			
24	1985.782	3.311	29.3	63	1066.837	1.779	17.5			
25	1954.044	3.258	28.6	64	1060.489	1.768	38.3			
26	1943.790	3.241	25.4	65	1059.025	1.766	37.5			
27	1868.595	3.116	15.4	66	1056.095	1.761	29.0			
28	1863.224	3.107	16.4	67	1049.747	1.750	16.2			
29	1856.388	3.095	16.7	68	1045.353	1.743	17.3			
30	1851.017	3.086	15.8	69	1042.423	1.738	7.8			
31	1414.982	2.359	21.5	70	1035.587	1.727	7.5			
32	1403.751	2.340	23.7	71	995.548	1.660	15.0			
33	1396.427	2.328	25.2	72	983.829	1.640	13.9			
34	1384.708	2.309	25.4	73	814.884	1.359	18.5			
35	1227.482	2.047	11.9	74	811.466	1.353	15.3			
36	1225.040	2.043	12.7	75	799.747	1.333	23.3			
37	1221.622	2.037	8.2	76	797.794	1.330	19.2			
38	1219.181	2.033	8.4	77	788.517	1.315	15.5			
39	1216.739	2.029	8.6	78	785.587	1.310	15.4			



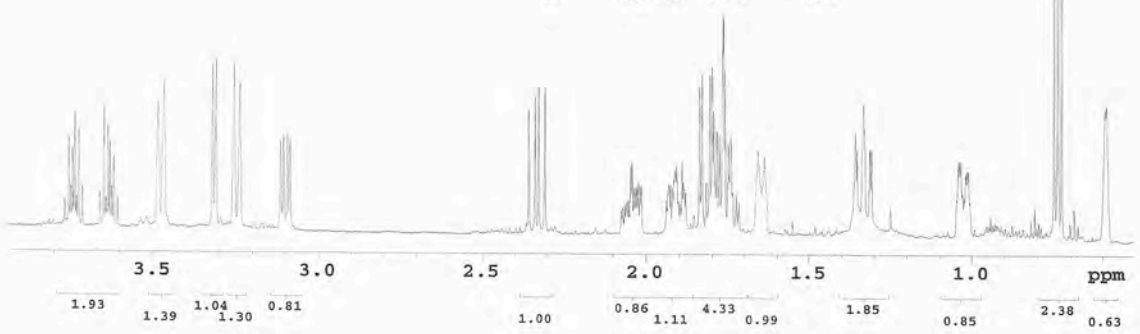
JGMM-XIV-2011 - R3 alkyne DA

expl PROTON

SAMPLE		DEC. & VT	
date	Feb 22 2008	dfrq	599.776
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
JasonMCharacteriza~		dof	0
tion/JGMM-Char-XIV~		dm	nnn
	-2011.fid	dmm	c
ACQUISITION		dmf	200
sfrq	599.776	dseq	
tn	H1	dres	1.0
at	1.892	homo	n
np	30272	temp	25.0
sw	8000.0	PROCESSING	
fb	not used	wtfile	
bs	2	proc	ft
tpwr	59	fn	not used
pw	5.5	math	f
d1	0		
tof	0	werr	
nt	3200	wexp	wft
ct	136	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	303.2		
wp	2058.6		
vs	824		
sc	35		
wc	215		
hzmm	9.56		
is	33.57		
rfl	5266.1		
rfp	4294.4		
th	10		
ins	1.000		
nm	ph		



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2252.872	3.756	16.8	40	1045.353	1.743	17.4
2	2246.036	3.745	14.6	41	995.548	1.660	14.7
3	2242.130	3.738	21.6	42	983.829	1.640	13.6
4	2234.806	3.726	18.4	43	814.884	1.359	18.5
5	2188.907	3.650	22.7	44	811.466	1.353	14.9
6	2181.583	3.637	19.2	45	799.747	1.333	23.7
7	2178.165	3.632	16.2	46	797.794	1.330	19.2
8	2170.841	3.619	13.4	47	788.517	1.315	15.0
9	2091.251	3.487	23.7	48	785.587	1.310	14.9
10	2080.997	3.470	27.7	49	624.943	1.042	12.3
11	1992.130	3.321	31.1	50	622.501	1.038	12.8
12	1985.782	3.311	31.9	51	620.060	1.034	12.7
13	1954.044	3.258	31.1	52	611.271	1.019	10.5
14	1943.790	3.241	27.5	53	608.829	1.015	10.9
15	1868.595	3.116	16.3	54	605.900	1.010	11.0
16	1863.224	3.107	17.4	55	450.626	0.751	72.7
17	1856.388	3.095	17.7	56	443.790	0.740	123.3
18	1851.017	3.086	16.8	57	436.466	0.728	72.0
19	1414.982	2.359	22.5	58	355.900	0.593	22.7
20	1403.751	2.340	24.9	59	353.458	0.589	23.5
21	1396.427	2.328	26.6				
22	1384.708	2.309	26.9				
23	1227.482	2.047	11.6				
24	1225.040	2.043	12.5				
25	1147.404	1.913	11.0				
26	1146.427	1.911	10.5				
27	1144.962	1.909	11.7				
28	1135.197	1.893	12.4				
29	1103.458	1.840	26.8				
30	1099.064	1.832	29.5				
31	1084.904	1.809	29.3				
32	1080.509	1.802	31.0				
33	1077.579	1.797	22.4				
34	1071.720	1.787	18.4				
35	1066.837	1.779	17.6				
36	1060.489	1.768	40.8				
37	1059.025	1.766	39.9				
38	1056.095	1.761	30.4				
39	1049.747	1.750	16.1				



JGMM-XIV-2053b - Recovered R3 vinyl brom
ide

exp2 PROTON

SAMPLE		DEC. & VT	
date	Mar 31 2008	dfrq	599.776
solvent	Benzene	dn	H1
file	/data/jasonm/-	dpwr	30
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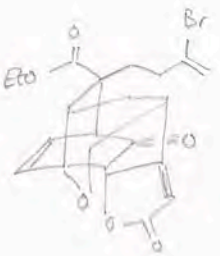
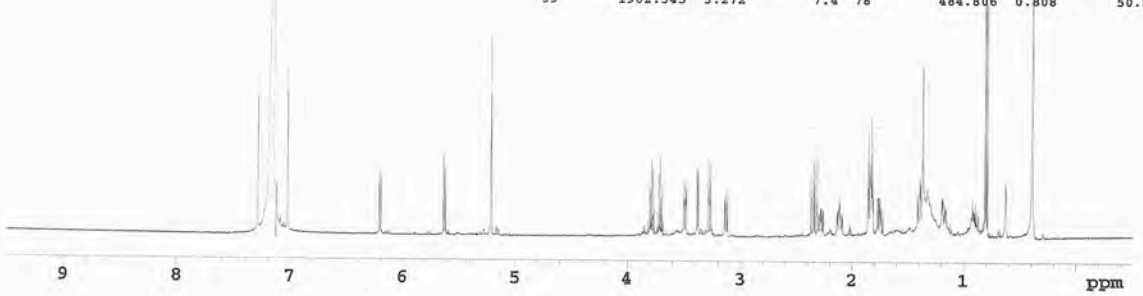
	XIV-2053b.fid	dm	nnn
ACQUISITION		dmm	c
sfrq	599.776	dmf	200
tn	H1	dseq	
at	1.892	dres	1.0
np	30272	homo	n
sw	8000.0	PROCESSING	
fb	not used	wtfile	
bs	2	proc	ft
tpwr	59	fn	not used
pw	5.5	math	f
dl	0		
tof	0	werr	
nt	320	wexp	wft
ct	46	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-300.4		
wp	5997.6		
vs	4717		
sc	35		
wc	215		
hzmm	27.86		
is	33.57		
rfl	5266.6		
rfp	4294.4		
th	6		
ins	1.000		
nm	ph		

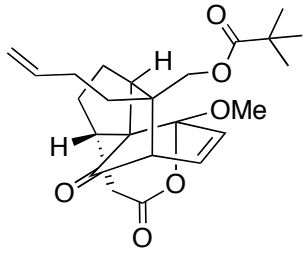


INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM
1	4372.013	7.289	30.1	40	1960.880	3.269	13.4	79	477.482	0.796
2	4294.376	7.160	4717.0	41	1958.927	3.266	7.1	80	470.646	0.785
3	4271.427	7.122	9.4	42	1885.685	3.144	7.9	81	377.872	0.630
4	4272.404	7.123	9.7	43	1880.314	3.135	8.6	82	374.943	0.625
5	4213.810	7.026	31.7	44	1873.478	3.124	8.7	83	232.853	0.388
6	3726.993	6.214	11.9	45	1868.107	3.115	7.9			
7	3725.529	6.212	10.8	46	1418.400	2.365	11.1			
8	3718.204	6.199	10.5	47	1406.193	2.345	14.7			
9	3717.228	6.198	12.3	48	1398.868	2.332	14.9			
10	3383.243	5.641	14.7	49	1386.661	2.312	14.9			
11	3376.896	5.630	15.2	50	1266.544	2.112	8.0			
12	3374.943	5.627	12.1	51	1112.247	1.854	14.3			
13	3368.595	5.616	12.5	52	1107.853	1.847	19.9			
14	3130.802	5.220	17.6	53	1101.505	1.837	11.2			
15	3128.849	5.217	38.1	54	1099.552	1.833	13.6			
16	3126.407	5.213	26.8	55	1096.622	1.828	9.8			
17	3125.431	5.211	17.5	56	1092.716	1.822	23.0			
18	2281.193	3.803	9.1	57	1088.322	1.815	18.4			
19	2274.357	3.792	8.5	58	1084.415	1.808	7.9			
20	2270.450	3.786	14.1	59	1062.931	1.772	7.5			
21	2263.614	3.774	12.5	60	1057.072	1.762	7.5			
22	2232.853	3.723	11.2	61	1050.724	1.752	7.2			
23	2225.529	3.711	14.7	62	1045.353	1.743	7.0			
24	2222.111	3.705	7.0	63	848.087	1.414	7.2			
25	2214.786	3.693	9.2	64	844.669	1.408	8.0			
26	2102.482	3.505	6.6	65	835.880	1.394	8.8			
27	2100.040	3.501	9.7	66	833.927	1.390	11.4			
28	2097.599	3.497	6.5	67	832.462	1.388	10.3			
29	2092.228	3.488	8.0	68	830.509	1.385	9.9			
30	2090.275	3.485	10.7	69	821.720	1.370	14.8			
31	2087.833	3.481	6.9	70	817.814	1.364	32.6			
32	2032.169	3.388	12.5	71	804.142	1.341	7.6			
33	2031.193	3.387	12.2	72	792.423	1.321	8.9			
34	2025.822	3.378	12.7	73	715.275	1.193	7.6			
35	2024.845	3.376	12.0	74	712.833	1.189	7.3			
36	1972.599	3.289	8.9	75	709.904	1.184	7.0			
37	1970.646	3.286	14.7	76	552.189	0.921	6.9			
38	1969.181	3.283	7.8	77	534.611	0.891	6.2			
39	1962.345	3.272	7.4	78	484.806	0.808	50.6			



A2.3 Crystal Structure Data for [5+2] Adduct.

Crystals of a pivaloate derivative of **2.22**, called **2.22piv**, were grown from DCM/hexanes and analyzed by X-ray crystallography.



2.22piv

Figure A2.1. Pivaloate derivative of **2.22**, drawn as the enantiomer of the representation shown in paper.

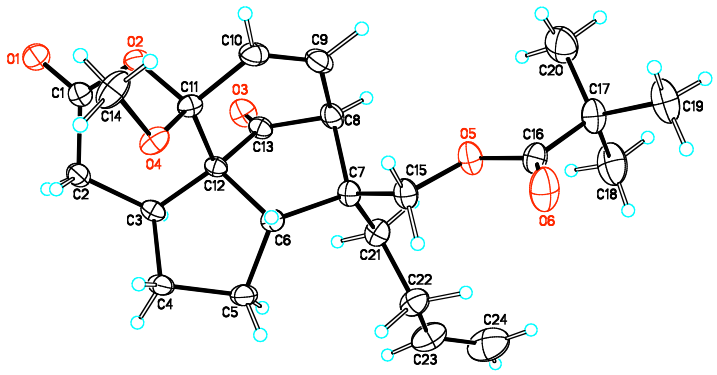


Figure A2.2. ORTEP diagram of **2.22piv**.

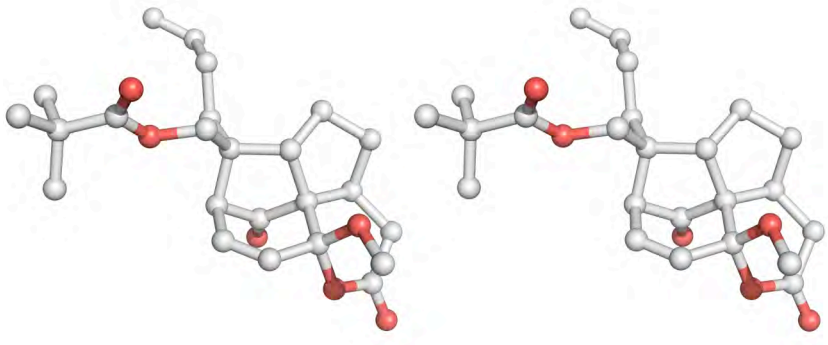


Figure A2.3. Stereoview of **2.22piv**.

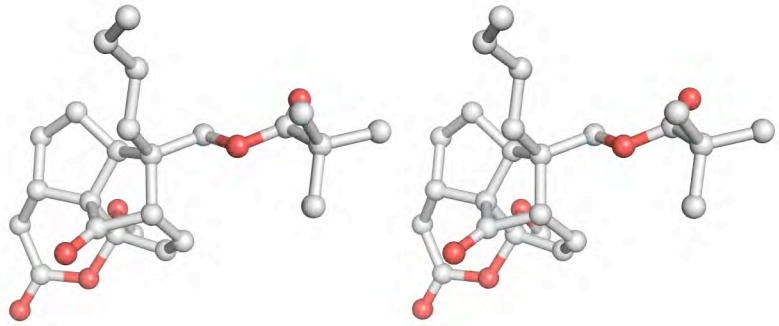


Figure A2.4. Another stereoview of **2.22piv**.

Table A2.1. Crystal data and structure refinement for **2.22piv**

Empirical formula	C24 H32 O6	
Formula weight	416.50	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 24.0661(18) Å	a = 90°
	b = 7.9489(6) Å	b = 99.112(4)°
	c = 11.9149(9) Å	g = 90°
Volume	2250.5(3) $Å^3$	
Z	4	
Density (calculated)	1.229 Mg/m^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	896	
Crystal size	0.60 x 0.50 x 0.20 mm^3	
Theta range for data collection	1.71 to 28.28°.	
Index ranges	-32<=h<=32, -10<=k<=10, -15<=l<=15	
Reflections collected	47029	
Independent reflections	5587 [R(int) = 0.0316]	
Completeness to theta = 28.28°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9828 and 0.9495	
Refinement method	Full-matrix least-squares on F^2	

Table A2.1 (Continued)

Data / restraints / parameters	5587 / 0 / 399
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1366
R indices (all data)	R1 = 0.0586, wR2 = 0.1442
Largest diff. peak and hole	0.534 and -0.252 e.Å^{-3}

Table A2.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **2.22piv**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4728(1)	2982(1)	5909(1)	33(1)
O(2)	3965(1)	3575(1)	6627(1)	25(1)
O(3)	3200(1)	5317(1)	4423(1)	33(1)
O(4)	3966(1)	5407(1)	8160(1)	28(1)
O(5)	1653(1)	7322(1)	6717(1)	34(1)
O(6)	1315(1)	8144(2)	8265(1)	49(1)
C(1)	4449(1)	4062(1)	6258(1)	24(1)
C(2)	4598(1)	5894(1)	6342(1)	27(1)
C(3)	4094(1)	7091(1)	6069(1)	23(1)
C(4)	4154(1)	8752(1)	6741(1)	27(1)
C(5)	3550(1)	9385(1)	6662(1)	29(1)
C(6)	3218(1)	7791(1)	6860(1)	22(1)
C(7)	2582(1)	7601(1)	6311(1)	25(1)
C(8)	2562(1)	5779(2)	5810(1)	28(1)
C(9)	2618(1)	4446(2)	6722(1)	33(1)
C(10)	3108(1)	3998(1)	7315(1)	31(1)
C(11)	3649(1)	4836(1)	7146(1)	23(1)
C(12)	3543(1)	6356(1)	6348(1)	20(1)
C(13)	3114(1)	5726(1)	5352(1)	25(1)

Table A2.2 (Continued)

C(14)	4171(1)	4149(2)	8982(1)	40(1)
C(15)	2218(1)	7760(2)	7234(1)	29(1)
C(16)	1240(1)	7547(2)	7330(1)	29(1)
C(17)	679(1)	6954(2)	6669(1)	36(1)
C(18)	498(1)	8241(3)	5729(1)	54(1)
C(19)	246(1)	6876(3)	7473(1)	53(1)
C(20)	750(1)	5225(2)	6148(2)	57(1)
C(21)	2378(1)	8784(2)	5310(1)	30(1)
C(22)	2220(1)	10563(2)	5631(1)	38(1)
C(23)	2102(1)	11699(2)	4622(1)	50(1)
C(24)	1604(1)	12299(2)	4188(2)	71(1)

Table A2.3. Bond lengths [Å] and angles [°] for **2.22piv**.

O(1)-C(1)	1.2043(13)
O(2)-C(1)	1.3655(13)
O(2)-C(11)	1.4539(12)
O(3)-C(13)	1.2021(13)
O(4)-C(11)	1.3978(12)
O(4)-C(14)	1.4323(14)
O(5)-C(16)	1.3349(14)
O(5)-C(15)	1.4444(13)
O(6)-C(16)	1.1983(14)
C(1)-C(2)	1.4999(15)
C(2)-C(3)	1.5357(15)
C(3)-C(12)	1.5330(14)
C(3)-C(4)	1.5389(15)
C(4)-C(5)	1.5287(16)
C(5)-C(6)	1.5357(15)
C(6)-C(12)	1.5609(14)
C(6)-C(7)	1.5747(14)
C(7)-C(15)	1.5153(15)

Table A2.3 (Continued)

C(7)-C(21)	1.5365(15)
C(7)-C(8)	1.5648(16)
C(8)-C(9)	1.5087(17)
C(8)-C(13)	1.5150(15)
C(9)-C(10)	1.3223(17)
C(10)-C(11)	1.5055(15)
C(11)-C(12)	1.5332(14)
C(12)-C(13)	1.5294(13)
C(16)-C(17)	1.5250(16)
C(17)-C(19)	1.5248(19)
C(17)-C(20)	1.528(2)
C(17)-C(18)	1.529(2)
C(21)-C(22)	1.5278(18)
C(22)-C(23)	1.4941(19)
C(23)-C(24)	1.318(3)
C(1)-O(2)-C(11)	118.11(8)
C(11)-O(4)-C(14)	116.53(9)
C(16)-O(5)-C(15)	117.90(9)
O(1)-C(1)-O(2)	117.44(10)
O(1)-C(1)-C(2)	125.03(10)
O(2)-C(1)-C(2)	117.51(9)
C(1)-C(2)-C(3)	114.51(9)
C(12)-C(3)-C(2)	113.50(9)
C(12)-C(3)-C(4)	103.14(8)
C(2)-C(3)-C(4)	114.53(8)
C(5)-C(4)-C(3)	103.91(8)
C(4)-C(5)-C(6)	103.35(9)
C(5)-C(6)-C(12)	103.80(8)
C(5)-C(6)-C(7)	120.66(9)
C(12)-C(6)-C(7)	106.43(8)
C(15)-C(7)-C(21)	111.20(9)
C(15)-C(7)-C(8)	111.60(9)

Table A2.3 (Continued)

C(21)-C(7)-C(8)	106.46(8)
C(15)-C(7)-C(6)	109.06(8)
C(21)-C(7)-C(6)	115.73(9)
C(8)-C(7)-C(6)	102.47(8)
C(9)-C(8)-C(13)	104.84(9)
C(9)-C(8)-C(7)	112.41(9)
C(13)-C(8)-C(7)	100.82(8)
C(10)-C(9)-C(8)	123.00(10)
C(9)-C(10)-C(11)	121.75(10)
O(4)-C(11)-O(2)	110.02(8)
O(4)-C(11)-C(10)	113.15(9)
O(2)-C(11)-C(10)	105.84(8)
O(4)-C(11)-C(12)	107.12(8)
O(2)-C(11)-C(12)	109.01(8)
C(10)-C(11)-C(12)	111.66(9)
C(13)-C(12)-C(3)	117.21(8)
C(13)-C(12)-C(11)	104.42(8)
C(3)-C(12)-C(11)	111.78(8)
C(13)-C(12)-C(6)	102.92(8)
C(3)-C(12)-C(6)	108.07(8)
C(11)-C(12)-C(6)	112.20(8)
O(3)-C(13)-C(8)	128.80(10)
O(3)-C(13)-C(12)	127.62(10)
C(8)-C(13)-C(12)	103.57(8)
O(5)-C(15)-C(7)	106.52(8)
O(6)-C(16)-O(5)	122.99(11)
O(6)-C(16)-C(17)	126.45(11)
O(5)-C(16)-C(17)	110.55(9)
C(19)-C(17)-C(16)	108.97(10)
C(19)-C(17)-C(20)	110.49(13)
C(16)-C(17)-C(20)	109.95(11)
C(19)-C(17)-C(18)	110.09(12)
C(16)-C(17)-C(18)	107.30(11)

Table A2.3 (Continued)

C(20)-C(17)-C(18)	109.98(13)
C(22)-C(21)-C(7)	115.70(9)
C(23)-C(22)-C(21)	112.44(11)
C(24)-C(23)-C(22)	125.48(17)

Table A2.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2.22piv**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	34(1)	32(1)	35(1)	-10(1)	10(1)	1(1)
O(2)	30(1)	20(1)	27(1)	-2(1)	10(1)	-1(1)
O(3)	35(1)	42(1)	21(1)	-7(1)	3(1)	-4(1)
O(4)	38(1)	27(1)	18(1)	2(1)	0(1)	7(1)
O(5)	24(1)	51(1)	26(1)	-9(1)	5(1)	-3(1)
O(6)	36(1)	80(1)	33(1)	-17(1)	7(1)	4(1)
C(1)	26(1)	27(1)	20(1)	-4(1)	3(1)	-1(1)
C(2)	24(1)	28(1)	30(1)	-5(1)	6(1)	-4(1)
C(3)	25(1)	23(1)	21(1)	1(1)	4(1)	-6(1)
C(4)	29(1)	20(1)	30(1)	0(1)	2(1)	-6(1)
C(5)	33(1)	20(1)	33(1)	1(1)	1(1)	-2(1)
C(6)	24(1)	22(1)	20(1)	0(1)	0(1)	0(1)
C(7)	23(1)	30(1)	20(1)	-1(1)	1(1)	1(1)
C(8)	23(1)	34(1)	27(1)	-7(1)	1(1)	-5(1)
C(9)	32(1)	29(1)	40(1)	-6(1)	15(1)	-9(1)
C(10)	38(1)	24(1)	34(1)	1(1)	16(1)	-4(1)
C(11)	28(1)	21(1)	21(1)	0(1)	7(1)	1(1)
C(12)	22(1)	20(1)	18(1)	0(1)	2(1)	-3(1)
C(13)	26(1)	25(1)	22(1)	-2(1)	1(1)	-4(1)
C(14)	52(1)	43(1)	24(1)	9(1)	6(1)	21(1)
C(15)	23(1)	40(1)	22(1)	-3(1)	1(1)	0(1)
C(16)	27(1)	36(1)	24(1)	2(1)	4(1)	6(1)

Table A2.4 (Continued)

C(17)	26(1)	52(1)	29(1)	0(1)	4(1)	3(1)
C(18)	36(1)	83(1)	41(1)	17(1)	-4(1)	8(1)
C(19)	32(1)	84(1)	44(1)	1(1)	11(1)	-5(1)
C(20)	42(1)	63(1)	62(1)	-23(1)	1(1)	-9(1)
C(21)	31(1)	35(1)	22(1)	0(1)	-1(1)	4(1)
C(22)	42(1)	35(1)	33(1)	-3(1)	-2(1)	7(1)
C(23)	69(1)	36(1)	46(1)	5(1)	10(1)	11(1)
C(24)	90(1)	50(1)	62(1)	10(1)	-17(1)	16(1)

Table A2.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2.22piv**.

	x	y	z	U(eq)
H(2B)	4875(6)	6095(19)	5866(12)	37(4)
H(2A)	4769(6)	6068(18)	7087(12)	32(3)
H(3)	4037(5)	7315(16)	5243(11)	24(3)
H(4B)	4310(6)	8510(18)	7526(12)	33(3)
H(4A)	4400(6)	9558(18)	6441(11)	30(3)
H(5B)	3501(6)	10260(20)	7196(12)	39(4)
H(5A)	3417(6)	9904(19)	5904(12)	33(3)
H(6)	3246(5)	7616(16)	7696(11)	21(3)
H(8)	2238(5)	5545(16)	5251(11)	26(3)
H(9)	2262(6)	3930(20)	6839(13)	42(4)
H(10)	3126(6)	3110(20)	7870(12)	38(4)
H(14C)	4347(8)	3290(20)	8638(16)	60(5)
H(14B)	3878(8)	3740(30)	9386(17)	69(6)
H(14A)	4438(8)	4720(30)	9565(16)	67(5)
H(15B)	2228(5)	8869(18)	7545(11)	27(3)
H(15A)	2336(5)	6940(17)	7854(11)	25(3)
H(18C)	490(8)	9340(30)	6073(16)	66(6)
H(18B)	754(8)	8270(30)	5143(17)	69(6)

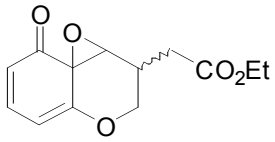
Table A2.5 (Continued)

H(18A)	135(9)	7840(30)	5325(17)	74(6)
H(19C)	363(8)	6060(30)	8089(17)	66(5)
H(19B)	-132(8)	6600(30)	7047(16)	68(6)
H(19A)	218(8)	7960(30)	7854(17)	70(6)
H(20C)	373(8)	4790(30)	5746(17)	74(6)
H(20B)	1003(7)	5330(20)	5579(15)	59(5)
H(20A)	917(9)	4430(30)	6740(19)	81(7)
H(21B)	2021(6)	8291(19)	4855(12)	38(4)
H(21A)	2682(6)	8882(19)	4802(12)	35(4)
H(22B)	1838(6)	10490(20)	6007(13)	44(4)
H(22A)	2554(7)	10960(20)	6200(14)	47(4)
H(23)	2449(9)	12020(30)	4314(18)	81(7)
H(24B)	1523(10)	13010(30)	3490(20)	91(7)
H(24A)	1274(12)	12030(40)	4630(20)	117(9)

APPENDIX 3

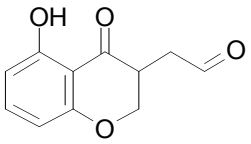
A3.1 Experimental Procedures for Chapter 3

General Information: Commercial reagents were purchased and used without further purification. Toluene, dichloromethane, benzene, and THF were dried over a column of alumina prior to use. Flash chromatography was performed with MP Silitech 32-63D 60Å silica, while thin layer chromatography (TLC) was performed with EMD 250 μm silica gel 60-F_{254} plates. NMRs were acquired on Varian Mercury 300 or Inova 500 or 600 MHz spectrometers and referenced to residual protic solvent. IR spectroscopic information was collected on a Nicolet Avatar 370 OTGS spectrometer. High-resolution mass spectrometry was obtained at the University of Illinois at Urbana-Champaign facility or Cornell University facility.

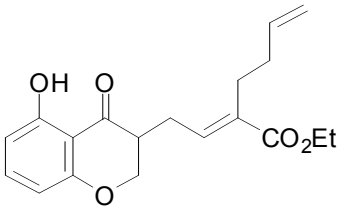


Ethyl 2-(2-oxo-2,7,8,8a-tetrahydrooxireno[2,3-d]chromen-8-yl)acetate (3.2): Ethyl 2-(5-hydroxy-4-oxochroman-3-yl)acetate **(3.1)** (61 mg, 0.244 mmol, 1.0 eq.) was dissolved in MeOH with mechanical stirring at 0 ºC and $NaBH_4$ (13.8 mg, 0.366 mmol, 1.5 eq.) was added. The reaction mixture was stirred for 45 min, then quenched with 0.4 ml 1M HCl. Stirring at 0 ºC continued for 30 min, after which time water was added and the mixture extracted with EtOAc (x3). The combined organic layers were washed with brine, then dried with Na_2SO_4 and concentrated *in vacuo*. The crude diol was then dissolved in 1.2 ml MeOH and 1.2 ml H_2O with mechanical stirring. $NaIO_4$ (78.3 mg, 0.366 mmol, 1.5 eq.) was added and the reaction mixture immediately became a bright yellow. Stirring was continued for 0.5 h, after which time water was added and the organic layer separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 20% EtOAc/Hex) afforded the product as a 2.7:1 mixture of diastereomeric spiroquinols (52.2 mg, 86% yield) appearing as a bright yellow oil. No effort was made to seaparate the diastereomers. **Major diastereomer**: ^{1}H-NMR (400 MHz, C_6D_6) δ 6.43 (dd, *J*=7.17, 9.76), 5.75 (d, *J*=9.80, 1H), 5.41(d, *J*=7.16. 1H), 4.04 (dd, *J*=3.04, 11.19, 1H), 3.92 (dd, *J*=1.31, 2.44, 1H), 3.86-3.99 (m, 2H), 3.65-3.45 (m, 2H), 2.22 (ddtd, *J*=1.20, 2.83, 2.81, 5.53, 8.52, 1H), 1.86 (dd, *J*=8.76, 16.71, 1H), 1.68 (dd, *J*=5.60, 16.70, 1H), 0.85 (t, *J*=7.12, 2H); ^{13}C-NMR (126 MHz, C_6D_6) δ 190.45, 170.24, 159.59, 144.29, 118.69, 102.91, 65.48, 62.89, 60.60, 53.62, 31.61, 31.58, 14.00. **Minor diastereomer:** ^{1}H-NMR (400 MHz, C_6D_6) δ 6.45 (dd, *J*=7.18, 9.76, 1H), 5.76 (d, *J*=9.79, 1H), 5.47 (d, *J*=7.15, 1H), 4.04 (dd, *J*=3.04, 11.19, 1H), 3.96 (bs, 1H), 3.86-3.99 (m, 2H), 3.65-3.45 (m, 2H), 2.08 (dtd, *J*=5.31, 7.13, 7.12, 12.21, 1H), 1.87 (dd, *J*=7.09, 16.62, 1H), 1.60 (dd, *J*=7.12, 16.64. 1H), 0.88 (t, *J*=7.11, 3H); ^{13}C-

NMR (126 MHz, C_6D_6) δ 190.49, 170.06, 159.51, 144.22, 118.61, 103.20, 65.71, 62.75, 60.66, 54.39, 32.83, 31.63, 14.04; **Both:** FTIR (thin film/KCl) 2961, 2980, 2915, 1731, 1669, 1624, 1542, 1466, 1418, 1377, 1355, 1287, 1251, 1208, 1183, 1115, 1062, 1024, 794, 763 cm^{-1}; HRMS (EI) *m/z* found 250.0840 [calc'd for $C_{13}H_{14}O_5$: 250.0841].

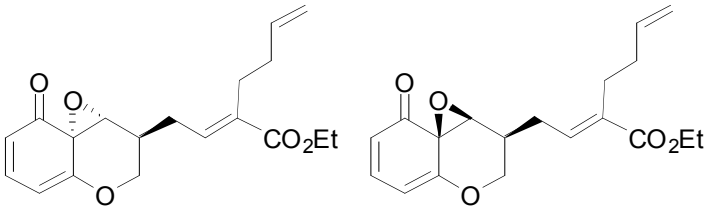


2-(5-Hydroxy-4-oxochroman-3-yl)acetaldehyde (3.4): In a flame-dried flask under N_2 atmosphere was dissolved ethyl 2-(5-hydroxy-4-oxochroman-3-yl)acetate (**2.27**) (1.39 g, 5.55 mmol, 1.0 eq.) in anhydrous PhMe with magnetic stirring. The solution was brought to –78 ºC and DIBAL-H (12.22 ml of a 1.0 M soln. in PhMe, 12.22 mmol, 2.2 eq.) was added over 8 h via syringe pump. The reaction was allowed to stir an additional 1 h, then quenched with 55 ml 1.0 M HCl and brought to ambient temperature. Stirring was continued for another 2 h, then the reaction mixture was separated with EtOAc (x3), dried with Na_2SO_4, and concentrated *in vacuo*. Column chromatography (SiO_2; 10 → 20 → 30% EtOAc/Hex) provided the aldehyde **3.4** (709 mg, 61% yield) as a white solid. ^{1}H-NMR (400 MHz, C_6D_6) δ 12.06 (s, 1H), 9.00 (s, 1), 6.88 (t, *J* = 8.3, 1H), 6.50 (d, *J* = 8.3, 1H), 6.27 (d, *J* = 8.3, 1H), 3.71 (dd, *J* = 5.5, 11.0, 1H), 3.37 (t, *J* = 11.5, 1H), 2.77 – 2.67 (m, 1H), 2.10 (dd, *J* = 4.9, 18.5, 1H), 1.43 (dd, *J* = 7.4, 18.5, 1H); ^{13}C-NMR (126 MHz, C_6D_6) δ 198.86, 197.20, 162.97, 161.99, 138.38, 109.63, 108.09, 107.22, 69.29, 39.72, 38.66; FTIR (thin film/KCl) 3085, 2889, 2847, 2734, 1724, 1643, 1627, 1578, 1462, 1392, 1362, 1160, 1066, 1003, 802, 731 cm^{-1}; HRMS (EI) *m/z* found 206.0577 [calc'd for $C_{11}H_{10}O_4$: 206.0579].



(E)-Ethyl 2-(2-(5-hydroxy-4-oxochroman-3-yl)ethylidene)hex-5-enoate (3.5): In a flame-dried flask under N_2 atmosphere with mechanical stirring was dissolved ethyl 2-(diethoxyphosphoryl)hex-5-enoate **(2.7)** (270 mg, 0.970 mmol, 2.0 eq.) in 2 ml anhydrous PhMe at 0 ºC. To this was added *t*-BuOK (103 mg, 0.922 mmol, 1.9 eq.) and the resulting yellow reaction mixture was allowed to stir 5 min, brought to ambient temperature for 10 min, then brought to –78 ºC. In a separate flame-dried flask under N_2 atmosphere was dissolved aldehyde **3.4** (100 mg, 0.485 mmol, 1.0 eq.) in 2.4 ml anhydrous PhMe with mechanical stirring at 0 ºC. To this was added *t*-BuOK , giving a yellow solution which was stirred an additional 10 min. A canula was then used to add this aldehyde solution to the phosphonate solution dropwise

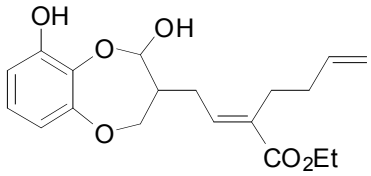
down the side of the flask. After 45 min, the reaction mixture was brought slowly to ambient temperature, at which point it became green. Saturated NH_4Cl was added, and after 10 min the reaction mixture became yellow. Extraction with EtOAc (x3), drying with Na_2SO_4, and concentration *in vacuo* was followed by column chromatography (SiO_2; 10-20% EtOAc/Hex) to provide **3.5** (120 mg, 75% yield as a 1:0.3 mixture of E:Z isomers) as a light yellow oil. ^{1}H-NMR (300 MHz, C_6D_6) δ 12.14 (s, 1H), 6.95 (t, *J* = 8.3, 1H), 6.67 (dd, *J* = 6.8, 8.4, 1H), 6.50 (d, *J* = 8.3, 1H), 6.28 (d, *J* = 8.2, 1H), 5.74 (ddt, *J* = 6.7, 10.1, 16.8, 1H), 4.97 (ddd, *J* = 1.3, 11.3, 13.7, 2H), 4.03 (q, *J* = 7.2, 2H), 3.75 (dd, *J* = 4.8, 11.4, 1H), 3.47 (dd, *J* = 9.4, 11.4, 1H), 2.46 – 2.27 (m, 3H), 2.24 – 2.07 (m, 3H), 1.96 (dt, *J* = 8.6, 15.2, 1H), 1.01 (t, *J* = 7.2, 3H); ^{13}C-NMR (75 MHz, C_6D_6) δ 199.25, 166.73, 163.15, 161.81, 138.30, 137.94, 137.92, 134.60, 115.36, 109.66, 108.08, 107.16, 69.26, 60.50, 44.61, 33.57, 26.61, 25.19, 14.28; FTIR (thin film/KCl) 3076, 2980, 2936, 2876, 1710, 1628, 1580, 1463, 1362, 1270, 1245, 1053, 1103, 916, 804, 745 cm^{-1}; HRMS (EI) *m/z* found 330.1470 [calc'd for $C_{19}H_{22}O_5$: 330.1467].



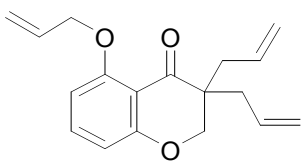
Desired **Undesired**

(E)-ethyl 2-(2-(2-oxo-2,7,8,8a-tetrahydrooxireno[2,3-d]chromen-8-yl)ethylidene)-hex-5-enoate (3.6): In a flask with magnetic stirring was dissolved phenol **3.5** (75.4 mg, 0.228 mmol, 1.0 eq.) in 2.3 ml MeOH at 0 ºC. $NaBH_4$ (13 mg, 0.34 mmol, 1.5 eq.) was added and the reaction mixture stirred 45 min. The reaction was quenched with 3 ml 1 M HCl, then brine was added and the mixture brought to ambient temperature. The organics were extracted with EtOAc (x3) and the combined organic layers were dried with Na_2SO_4 and dried *in vacuo*. The crude diol was redissolved in 1.1 ml MeOH and 1.1 ml H_2O and $NaIO_4$ (59 mg, 0.274 mmol, 1.2 eq.) was added. The reaction mixture immediately became yellow/orange. After 30 min it was diluted with H_2O and brine, then separated with EtOAc (x5). The organic layers were dried with Na_2SO_4, concentrated *in vacuo*, and subjected to column chromatography (SiO_2; 30% EtOAc/Hex) to provide the product quinols (60.3 mg, 80% yield) as a bright yellow 1:1 mixture of diastereomers. These diastereomers could in turn be separated by column chromatography using 20% EtOAc/30% DCM/50% Hex. **Desired diastereomer**: ^{1}H-NMR (400 MHz, C_6D_6) δ 6.56 (t, *J* = 7.6, 1H), 6.48 (dd, *J* = 7.2, 9.7, 1H), 5.79 (d, *J* = 9.7, 1H), 5.73 (ddt, *J* = 6.7, 10.1, 17.0, 1H), 5.49 (d, *J* = 7.2, 1H), 5.03 (ddd, *J* = 1.2, 11.1, 13.5, 2H), 4.04 (q, *J* = 7.2, 2H), 3.74 (s, 1H), 3.63 (t, *J* = 11.2, 1H), 3.30 (dd, *J* = 5.2, 10.6, 1H), 2.43 – 2.23 (m, 2H), 2.18 (dd, *J* = 7.0, 14.4, 2H),

1.77 (dt, *J* = 7.6, 15.2, 1H), 1.53 (dt, *J* = 7.0, 14.8, 1H), 1.42 – 1.22 (m, 1H), 0.99 (t, *J* = 7.1, 3H); ^{13}C-NMR (126 MHz, C_6D_6) δ 190.56, 166.68, 159.81, 144.27, 137.76, 137.06, 134.67, 118.57, 115.60, 103.03, 66.25, 62.99, 60.54, 54.55, 34.46, 33.53, 27.63, 26.59, 14.26. **Desired diastereomer**: ^{1}H-NMR (500 MHz, C_6D_6) δ 6.49 (dd, *J* = 6.7, 8.7, 1H), 6.45 (dd, *J* = 7.1, 9.8, 1H), 5.89 – 5.60 (m, 1H), 5.46 (d, *J* = 7.3, 1H), 5.12 – 4.85 (m, 2H), 4.02 (q, *J* = 7.1, 2H), 3.89 (dd, *J* = 3.2, 11.2, 1H), 3.79 (dd, *J* = 1.5, 2.4, 1H), 3.22 (t, *J* = 1.3, 1H), 2.39 – 2.23 (m, 2H), 2.24 – 2.06 (m, 2H), 1.72 (dt, *J* = 9.0, 14.6, 1H), 1.64 – 1.53 (m, 1H), 1.47 (dtd, *J* = 2.8, 5.4, 8.1, 1H), 0.98 (t, *J* = 7.2); ^{13}C-NMR (126 MHz, C_6D_6) δ 190.51, 166.68, 159.87, 144.37, 137.87, 137.35, 134.85, 118.71, 115.35, 102.75, 64.96, 63.54, 60.51, 53.95, 34.50, 33.59, 26.54, 26.37, 14.26; **Both:** FTIR (thin film/KCl) 3074, 2978, 2957, 2930, 2871, 1709, 1669, 1624, 1542, 1463, 1377, 1288, 1205, 1112, 1057, 911, 794, 762 cm^{-1}; HRMS (EI) *m/z* found 330.1468 [calc'd for $C_{19}H_{22}O_5$: 330.1467].

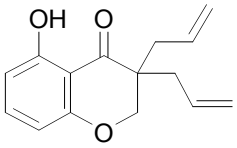


(E)-Ethyl 2-(2-(2,9-dihydroxy-3,4-dihydro-2H-benzo[b][1,4]dioxepin-3-yl)ethylidene)hex-5-enoate (3.8): In a flame-dried flask under N_2 atmosphere was dissolved **3.6** (4.1 mg, 12.4 μmol, 1.0 eq.) in 0.2 ml anhydrous PhMe. The solution was brought to –5 °C and a solutions of $EtAlCl_2$ (1.24 μl, 0.1 eq.) was added. After 1 h, another portion $EtAlCl_2$ (1.24 μl, 0.1 eq.) was added. The reaction mixture was stirred an additional 1.5 h, then quenched with sat. $NaHCO_3$. The reaction mixture was separated with EtOAc (x4) and the combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 10% EtOAc/Hex) provided **3.8** (2.2 mg, 54% yield) as an unstable yellow oil. ^{1}H-NMR (600 MHz, C_6D_6) δ 6.72 (dd, *J* = 1.6, 8.2, 1H), 6.71 – 6.65 (m, 2H), 6.56 (dd, *J* = 1.5, 8.1, 1H), 5.75 (ddt, *J* = 6.8, 10.2, 17.0, 1H), 5.51 (d, *J* = 3.6, 1H), 5.50 (s, 1H), 5.02 (ddd, *J* = 1.5, 3.1, 17.0, 1H), 4.95 – 4.91 (m, 1H), 4.08 (q, *J* = 7.1, 2H), 3.93 (dd, *J* = 1.3, 12.6, 1H), 3.71 (ddd, *J* = 1.0, 4.0, 12.7, 1H), 2.52 – 2.42 (m, 2H), 2.26 (ddd, *J* = 7.6, 14.9, 30.9, 3H), 2.17 – 2.10 (m, 1H), 1.71 – 1.66 (m, 1H), 1.03 (t, *J* = 7.1, 3H); ^{13}C-NMR (determined by HSQCAD, gHMBCAD) δ 166.8, 152.0, 151.5, 150.8, 137.5, 137.1, 135.2, 125.7, 115.1, 112.3, 110.4, 94.2, 67.6, 60.3, 48.6, 33.5, 27.8, 26.7, 14.1.

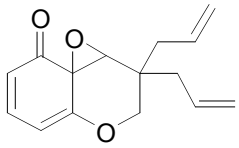


3,3-Diallyl-5-(allyloxy)chroman-4-one (3.10a): In a flame-dried flask under N_2

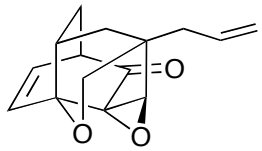
atmosphere was dissolved 5-hydroxychroman-4-one **(3.8)** (22 mg, 0.134 mmol, 1.0 eq.) in 0.45 ml anhydrous DMF. The addition of NaH (21 mg, 0.536 mmol of a 60% dispersion in mineral oil, 0.536 mmol, 4.0 eq.) with vigorous magnetic stirring resulted in a deep orange solution. After 5 min, allyl bromide (57 µl, 0.670 mmol, 5 eq.) was added and the reaction mixture brought to ambient temperature. After 4.5 h, the reaction mixture was quenched with a solution of saturated NH_4Cl, water, and was separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4, concentrated, and chromatographed (SiO_2; 10% EtOAc/Hex) to provide the triallylated product (36.8 mg, 97% yield) as a light yellow solid. ^{1}H-NMR (300 MHz, C_6D_6) δ 6.96 (t, *J* = 8.3, 1H), 6.58 (d, *J* = 8.3, 1H), 6.10 (d, *J* = 8.3, 1H), 5.84 (d, *J* = 5.1, 1H), 5.80 – 5.60 (m, 3H), 5.25 – 5.10 (m, 1H), 4.96 – 4.81 (m, 4H), 4.15 (s, 2H), 3.94 (s, 2H), 2.41 (dd, *J* = 7.4, 14.1, 2H), 2.23 (dd, *J* = 7.5, 14.0, 2H); ^{13}C-NMR (75 MHz, C_6D_6) δ 192.34, 163.20, 160.76, 135.10, 133.48, 132.73, 118.53, 116.91, 111.40, 109.94, 105.54, 72.80, 69.11, 48.08, 36.76; FTIR (thin film/KCl) 3075, 3008, 2978, 2914, 2864, 1683, 1638, 1601, 1575, 1473, 1450, 1329, 1251, 1119, 1092, 1070, 996, 918, 804, 763 cm^{-1}; HRMS (EI) *m/z* found 2484.1415 [calc'd for $C_{18}H_{20}O_3$: 284.1413].



3,3-Diallyl-5-hydroxychroman-4-one (3.10): To a flask under N_2 atmosphere with magnetic stirring was added 5-hydroxychroman-4-one **3.10a** (10.3 mg, 0.0362 mmol, 1.0 eq.) and $Pd(OAc)_2$ (0.8 mg, 4 µmol, 0.1 eq.) in 0.36 ml EtOH. Trifluoroacetic acid (4.2 µl, 0.054 mmol, 1.5 eq.) was added and the reaction mixture brought to 40 ºC. The reaction was monitored for completion by TLC, and after 3.5 h was diluted with water and brine, then separated with EtOAc (x4). The combined organic layers were dried with Na_2SO_4, then filtered through a short plug of Celite to remove residual palladium. Concentration *in vacuo* followed by chromatography (SiO_2; 10% EtOAc/Hex) gave the product (6.8 mg, 77% yield) as a yellow solid. ^{1}H-NMR (300 MHz, C_6D_6) δ 12.46 (s, 1H), 6.91 (t, *J* = 8.3, 1H), 6.54 (dd, *J* = 0.9, 8.3, 1H), 6.33 (dd, *J* = 0.9, 8.2, 1H), 5.51 (ddt, *J* = 7.4, 10.2, 17.5, 2H), 4.96-4.77 (m, 4H), 3.76 (s, 2H), 2.14 (ddd, *J* = 7.4, 14.1, 49.8, 4H); ^{13}C-NMR (75 MHz, C_6D_6) δ 216.36, 202.05, 163.70, 161.57, 138.21, 132.48,119.13, 109.88, 107.11, 72.67, 47.38, 36.34; FTIR (thin film/KCl) 3077, 3017, 2980, 2920, 1640, 1580, 1464, 1357, 1328, 1222, 1070, 1005, 921, 811, 750 cm^{-1}; HRMS (EI) *m/z* found 244.1094 [calc'd for $C_{15}H_{16}O_3$: 244.1100].

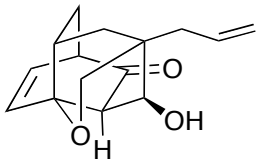


8,8-Diallyl-8,8a-dihydrooxireno[2,3-d]chromen-2(7H)-one (3.11): In a flame-dried flask under N_2 atmosphere with magnetic stirring were combined 3,3-diallyl-5-hydroxychroman-4-one (**3.10**) (11 mg, 0.045 mmol, 1.0 eq.) and $LiAlH_4$ (1.7 mg, 0.045 mmol, 1.0 eq.) in 0.45 mL anhydrous THF at 0 ºC. The reaction mixture flashes a bright yellow, then fades to a very slight yellow. After 10 min, 1M HCl was added and the mixture separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The resulting crude diol was then redissolved in 0.45 ml MeOH and 0.45 ml H_2O with magnetic stirring. $NaIO_4$ (11.6 mg, 0.54 mmol, 1.2 eq.) was added. The reaction mixture immediately became bright yellow and was allowed to stir 0.5 h, after which TLC indicated consumption of starting material. Note that the product spiroquinol is visibly yellow on the TLC plate. The reaction mixture was diluted with H_2O and separated with EtOAc (x3), dried with Na_2SO4_4, and subjected to chromatography (SiO_2; 20% EtOAc/Hex). The product was eluted as a visibly yellow band to provide spiroquinol **3.11** (9.3 mg, 85% yield) as a bright yellow oil. ^{1}H-NMR (500 MHz, C_6D_6) δ 6.48 (dd, *J* = 7.2, 9.8, 1H), 5.79 (d, *J* = 9.7, 1H), 5.50 (d, *J*=7.13, 1H), 5.46 (ddt, *J* = 7.5, 10.1, 17.5, 2H), 5.37 (ddt, *J* = 7.6, 10.1, 17.5, 1H), 4.94-4.78 (m, 4H), 3.88 (dd, *J* = 6.2, 10.6, 2H), 3.32 (dd, *J* = 1.5, 10.9, 1H), 1.79-1.62 (m, 4H); ^{13}C-NMR (126 MHz, C_6D_6) δ 190.71, 159.85, 144.42, 131.86, 131.67, 119.34, 119.30, 118.51, 102.92, 69.29, 66.48, 54.43, 38.86, 37.34, 35.94; FTIR (thin film/KCl) 3078, 3006, 2978, 2916, 2849, 1669, 1624, 1541, 1379, 1209, 1111, 1064, 996, 920, 796, 766 cm^{-1}; HRMS (EI) *m/z* found 244.1098 [calc'd for $C_{15}H_{16}O_3$: 244.1100].

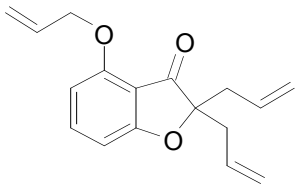


Bicycle 3.12: To a flame-dried pressure tube under N_2 atmosphere was added the quinol **3.11** (1.6 mg, 6.6 μmol) in 0.65 ml anhydrous and oxygen-free PhMe. The yellow solution was heated at 150 ºC overnight for 20 h, the yellow color fading slowly over this time. Cooling and concentration *in vacuo*, followed by chromatography (SiO_2; 10-20-30% EtOAc/Hex) provided the bicyclic **3.12** (1.4 mg, 88%) as a white solid. ^{1}H-NMR (600 MHz, C_6D_6) δ 6.25 (dd, *J* = 1.3, 8.4, 1H), 5.56 (dd, *J* = 7.0, 8.1, 1H), 5.46-5.31 (m, 1H), 4.95-4.85 (m, 1H), 4.79 (ddd, *J* = 1.5, 3.2, 16.9, 1H), 4.09 (dd, *J* = 3.2, 8.2, 1H), 3.14 (dd, *J* = 1.7, 8.2, 1H), 2.90- 2.87 (m, 1H), 2.89 (d, *J* = 1.69, 1H) 1.91-1.75 (m, 1H), 1.60-1.49 (m, 3H), 1.45 (dd, *J* = 9.6, 13.6, 1H), 0.91 (dt, *J* = 3.0, 13.6, 1H), 0.82 (ddd, *J* = 1.9, 4.4, 13.5, 1H); ^{13}C-NMR (determined by HSQCAD and gHMBCAD) δ 200.5, 136.9, 132.2, 124.2, 118.3, 74.9,

70.3, 61.2, 59.7, 50.0, 38.5, 38.3, 37.2, 36.2, 34.9; FTIR (thin film/KCl) 2985, 2917, 2866, 1735, 1717, 1559, 1541, 1521, 1457, 1430, 1322, 1247, 1166, 1078, 996, 927 cm^{-1}; HRMS (EI) *m/z* found 244.1103 [calc'd for $C_{15}H_{16}O_3$: 244.1100].

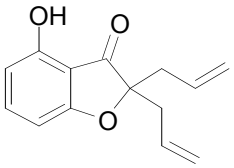


Bicycle 3.13: In a flame-dried flask under N_2 atmosphere was dissolved epoxide **3.12** (0.7 mg, 2.9 μmol, 1.0 eq.) and 2,4-cyclohexadiene (2.7 μl, 28.7 μmol, 10 eq.) in 0.2 ml anhydrous THF. The reaction mixture was brought to –78 ºC and a solution of Cp_2TiCl (~0.5M in THF) was added dropwise with TLC monitoring until the starting material was consumed. The reaction was then quenched with sat. NaH_2PO_4 and quickly brought to ambient temperature. After stirring 5 min the reaction mixture was separated with EtOAc (x4) and the combined organic layers dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 20% EtOAc/Hex) then provided the desired alcohol **3.13** (0.6 mg, 86% yield). ^{1}H NMR (600 MHz, C_6D_6) δ 6.33 (dd, *J* = 1.1, 8.7, 1H), 5.60 (dd, *J* = 5.6, 8.5, 1H), 5.47 (ddt, *J* = 7.6, 10.3, 17.8, 1H), 4.95 – 4.91 (m, 1H), 4.89 – 4.84 (m, 1H), 4.13 (dd, *J* = 3.1, 8.7, 1H), 3.60 (t, *J* = 4.0, 1H), 3.38 (dd, *J* = 1.7, 8.8, 1H), 2.82 (dtd, *J* = 1.2, 2.9, 4.0, 1H), 2.21 (t, *J* = 2.9, 1H), 1.86 (dd, *J* = 7.3, 13.7, 1H), 1.76 (dddd, *J* = 3.2, 4.6, 6.3, 15.8, 1H), 1.59 (dd, *J* = 11.1, 13.9, 1H), 1.56 – 1.47 (m, 2H), 0.81 – 0.75 (m, 2H); ^{13}C-NMR (determined by HSQCAD and gHMBCAD) δ 200.5, 138.2, 133.0, 125.9, 117.7, 74.9, 71.9, 67.0, 57.2, 49.3, 38.2, 36.7, 36.5, 36.4, 31.8;

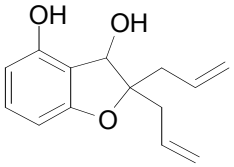


2,2-Diallyl-4-(allyloxy)benzofuran-3(2H)-one (3.15a): In a flame-dried flask under N_2 atmosphere was dissolved 4-hydroxybenzofuran-3(2H)-one **(3.14)** (51.8 mg, 0.345 mmol, 1.0 eq.) in 1.0 ml anhydrous DMF. The addition of NaH (55 mg of a 60% dispersion in mineral oil, 1.38 mmol, 4.0 eq.) with vigorous magnetic stirring resulted in a deep green solution. After 5 min, allyl bromide (150 μl, 1.38 mmol, 5 eq.) was added and the reaction mixture brought to ambient temperature. After 8 h, the reaction mixture was quenched with a solution of saturated NH_4Cl, water, and was separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4, concentrated, and chromatographed (SiO_2; 10-20% EtOAc/Hex) to provide the triallylated product (64.7 mg, 97% yield) as a pale yellow solid. ^{1}H-NMR (500 MHz, C_6D_6) δ 7.16 (s, 1H), 7.02 (t, *J* = 8.3, 1H), 6.53 (d, *J* = 8.3, 1H), 5.96 (d, *J* = 8.1, 1H),

5.82 – 5.53 (m, 3H), 5.41 (dq, *J* = 1.7, 17.3, 1H), 5.06 – 4.98 (m, 4H), 4.90-4.83 (m, 2H), 4.14 (dt, *J* = 1.6, 4.9, 2H), 2.56 – 2.31 (m, 4H); ^{13}C-NMR (126 MHz, C_6D_6) δ 198.80, 173.11, 157.41, 138.88, 132.52, 131.18, 119.58, 117.37, 111.68, 105.10, 104.49, 90.99, 69.14, 40.44; FTIR (thin film/KCl) 3079, 3014, 2983, 2912, 1713, 1642, 1606, 1491, 1446, 1337, 1263, 1240, 1116, 1086, 992, 923, 802, 764 cm^{-1}; HRMS (EI) *m/z* found 270.1259 [calc'd for $C_{17}H_{18}O_3$: 270.1256].

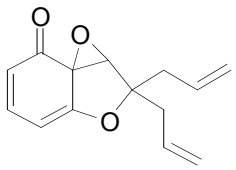


2,2-Diallyl-4-hydroxybenzofuran-3(2H)-one (3.15): To a flask under N_2 atmosphere with magnetic stirring was added **3.15a** (50.0 mg, 0.185 mmol, 1.0 eq.) and $Pd(OAc)_2$ (4.2 mg, 0.019 mmol, 0.1 eq.) in 2 ml EtOH. Acetic acid (15 µl, 0.278 mmol, 1.5 eq.) was added and the reaction mixture brought to 80 ºC. The reaction was monitored for completion by TLC, and after 3 h was diluted with water and brine, then separated with EtOAc (x4). The combined organic layers were dried with Na_2SO_4, then filtered through a short plug of Celite to remove residual palladium. Concentration *in vacuo* followed by chromatography (SiO_2; 15 → 20 → 30% EtOAc/Hex) gave the product (35.2 mg, 83% yield) as a yellow solid. ^{1}H-NMR (500 MHz, C_6D_6) δ 8.13 (s, 1H), 6.91 (t, *J* = 8.2, 1H), 6.31 (dd, *J* = 8.2, 14.3, 2H), 5.62 (ddt, *J* = 7.2, 10.0, 17.1, 2H), 4.98 (ddd, *J* = 1.5, 3.3, 17.1, 2H), 4.86 (ddt, *J* = 0.7, 1.7, 3.7, 2H), 2.56 – 2.21 (m, 4H). ^{13}C-NMR (126 MHz, C_6D_6) δ 204.03, 170.97, 156.95, 140.62, 130.63, 119.90, 109.84, 107.82, 103.65, 91.79, 39.79; FTIR (thin film/KCl) 3436, 3080, 2982, 2913, 1689, 1606, 1492, 1461, 1310, 1191, 1150, 1053, 986, 921, 804, 766 cm^{-1}; HRMS (EI) *m/z* found 230.0943 [calc'd for $C_{14}H_{14}O_3$: 230.0943].

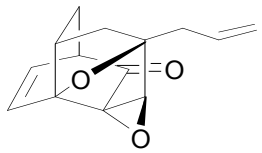


2,2-Diallyl-2,3-dihydrobenzofuran-3,4-diol (3.16a): In a flame-dried flask under N_2 atmosphere with magnetic stirring was dissolved hydroxybenzofuranone **3.15a** (21 mg, 0.0912 mmol, 1.0 eq.) in 0.9 ml anhydrous THF at 0 ºC. $LiAlH_4$ (4.1 mg, 0.109 mmol, 1.1 eq.) was added and the reaction briefly became green, then faded to yellow. Stirring was continued for 15 min., after which time the reaction was quenched with 1M HCl, brine, and separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*, then filtered through a plug of silica

with 30% EtOAc. The resultant diol (19.7 mg, 94%) was used without further purification. ^{1}H-NMR (400 MHz, C_6D_6) δ 6.93 (t, *J* = 8.1, 1H), 6.44 (d, *J* = 8.0, 1H), 6.31 (d, *J* = 8.0, 1H), 6.01 (ddt, *J* = 7.2, 10.1, 17.4, 1H), 5.68 (ddt, *J* = 7.2, 10.3, 17.3, 1H), 5.36 (s, 1H), 5.16 – 4.75 (m, 5H), 2.51 (ddd, *J* = 7.1, 14.4, 53.4, 2H), 2.22 (ddd, *J* = 7.1, 14.0, 36.1, 2H), 1.45 (d, *J* = 8.2, 1H).

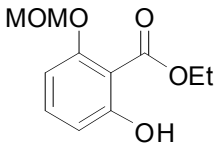


2,2-Diallyl-1aH-benzo[b]oxireno[2,3-c]furan-7(2H)-one (3.16): In a flask with magnetic stirring was dissolved diol **3.16a** (9.9 mg, 0.0426 mmol, 1.0 eq.) in 0.21 ml *i*-PrOH and 0.21 ml H_2O. $NaIO_4$ (13.7 mg, 0.0639 mmol, 1.5 eq.) was added and the reaction mixture allowed to stir overnight for 14 h. The reaction was diluted with H_2O and the organics extracted with EtOAc (x4). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 10 → 20 → 30 → 40% EtOAc/Hex) afforded 2.9 mg quinol **3.16** as a yellow oil and 4.4 mg recovered starting material **3.16** (30% yield, 71% B.R.S.M.). ^{1}H-NMR (400 MHz, C_6D_6) δ 6.38 (dd, *J* = 6.6, 9.9, 1H), 5.72 (d, *J* = 9.9, 1H), 5.56 (ddt, *J* = 7.4, 9.6, 17.2, 1H), 5.39 (ddt, *J* = 7.4, 10.3, 17.4, 1H), 5.17 (d, *J* = 6.6, 1H), 5.02 – 4.64 (m, 4H), 4.17 (s, 1H), 2.38 (qd, *J* = 7.5, 13.8, 2H), 1.92 (ddd, *J* = 7.3, 14.5, 65.3, 2H); ^{13}C-NMR (126 MHz, C_6D_6) δ 190.07, 164.63, 145.21, 131.90, 130.37, 120.20, 119.65, 119.44, 97.53, 90.09, 67.32, 60.65, 39.42, 37.99; FTIR (thin film/KCl) 3079, 2981, 2917, 2849, 1680, 1641, 1532, 1417, 1369, 1267, 1200, 1157, 1085, 980, 922, 868, 799, 780 cm^{-1}; HRMS (EI) *m/z* found 230.0943 [calc'd for $C_{14}H_{14}O_3$: 230.0943].

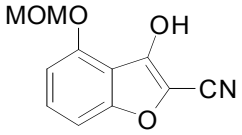


Bicycle 3.17: To a flame-dried pressure tube under N_2 atmosphere was added the quinol **3.16** (3.0 mg, 13 μmol) in 0.65 ml anhydrous and oxygen-free PhMe. The yellow solution was heated at 150 ºC overnight for 22 h, the yellow color fading slowly over this time. Cooling and concentration *in vacuo*, followed by chromatography (SiO_2; 20 → 30 → 40% EtOAc/Hex) provided the bicyclic **3.17** (0.60 mg, 20% yield) as a white solid. ^{1}H-NMR (600 MHz, C_6D_6) δ 6.41 (d, *J* = 8.8, 1H), 5.76 (ddt, *J* = 7.3, 10.5, 17.3, 1H), 5.45 (dd, *J* = 6.6, 8.5, 1H), 5.11 – 4.82 (m, 2H), 3.04 (s, 1H), 2.99 – 2.96 (m, 1H), 2.38 (qd, *J* = 7.1, 14.4, 2H), 1.64 (ddd, *J* = 5.4, 10.7,

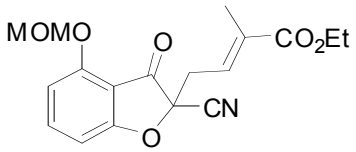
16.4, 1H), 1.39 (dd, *J* = 10.3, 12.5, 1H), 1.31 (ddd, *J* = 4.0, 11.6, 13.7, 1H), 1.09 (dd, *J* = 6.1, 13.4, 1H), 0.59 (dd, *J* = 4.6, 12.5, 1H); ^{13}C-NMR (determined by HSQCAD, gHMBCAD) δ 199.7, 132.1, 131.2, 125.3, 118.2, 89.1, 84.7, 60.5, 58.5, 51.1, 37.3, 35.7; FTIR (thin film/KCl) 3060, 2983, 2916, 2849, 1738, 1448, 1312, 1272, 972, 908, 817, 692, 624 cm^{-1}; HRMS (EI) *m/z* found 230.0942 [calc'd for $C_{14}H_{14}O_3$: 230.0943].



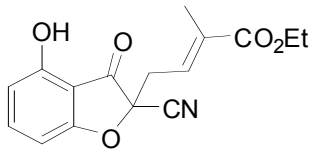
Ethyl 2-hydroxy-6-(methoxymethoxy)benzoate (3.21): In a flask with magnetic stirring was dissolved 5-(methoxymethoxy)-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one **(3.20)** (1.72 g, 7.22 mmol, 1.0 eq.) in 14 ml EtOH (stored over sieves). To this, K_2CO_3 (5.0 g, 36 mmol, 5.0 eq.) was added. The reaction mixture was stirred overnight at 45 °C, then the remaining solid K_2CO_3 filtered out through Celite. Aqueous extraction with brine and EtOAc (x3) was followed by drying of the combined organic layers with Na_2SO_4 and concentration *in vacuo* to give the product **3.21** (1.45 g, 89% yield) as a white solid which was used without further purification.



3-Hydroxy-4-(methoxymethoxy)benzofuran-2-carbonitrile (3.22): In a flame-dried flask under N_2 atmosphere was dissolved phenol **3.21** (216 mg, 0.955 mmol, 1.0 eq.) in 2 ml dry acetone. Chloroacetonitrile (0.12 ml, 1.91 mmol, 2.0 eq.) and K_2CO_3 (396 mg, 2.87 mmol, 3.0 eq.) were added and the mixture heated at 45 °C overnight. The reaction was then quenched with sat. NH_4Cl and separated with brine and EtOAc (x3). Drying of the combined organic layers with Na_2SO_4 and concentration *in vacuo* provided a dark red oil which was dissolved in 10 ml anhydrous PhH in a flame-dried flask under N_2 atmosphere with magnetic stirring. To this was added *t*-BuOK and the reaction mixture was stirred for 1 h. The reaction was quenched with 1M HCl and separated with EtOAc (x4). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (30 → 40 → 50% EtOAc/Hex) provided **3.22** (181 mg, 87% yield). ^{1}H-NMR (400 MHz, C_6D_6) δ **Enol form**: 6.78 (t, *J* = 8.3, 1H), 6.59 (d, *J* = 8.5, 1H), 6.50 (d, *J* = 8.0, 1H), , 4.44 (s, 2H), 2.87 (s, 3H); **Keto form**: 6.77 (t, *J* = 8.2, 1H), 6.33 (d, *J* = 8.3, 1H), 6.14 (d, *J* = 8.3, 1H) , 4.70 (s, 2H), 3.94 (s, 1H), 3.02 (s, 3H); FTIR (thin film/KCl) 3279, 2973, 2954, 2901, 2838, 2224, 1737, 1636, 1614, 1497, 1431, 1412, 1353, 1252, 1096, 1055, 923, 780, 737 cm^{-1}; HRMS (EI) *m/z* found 219.0529 [calc'd for $C_{11}H_9O_4N$: 219.0532].

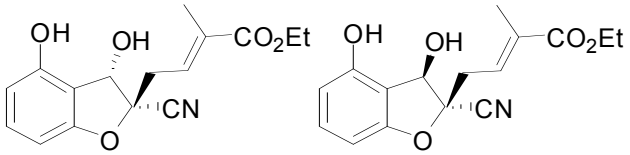


(E)-Ethyl 4-(2-cyano-4-(methoxymethoxy)-3-oxo-2,3-dihydrobenzofuran-2-yl)-2-methylbut-2-enoate (3.24): In a flame-dried flask under N_2 atmosphere was dissolved **3.22** (369 mg, 1.70 mmol, 1.0 eq.) in 17 ml anhydrous THF. In an additional flame-dried flask under N_2 atmosphere with magnetic stirring was washed NaH (102 mg of a 60% dispersion in mineral oil, 2.55 mmol, 1.5 eq.) with hexanes (x2), then suspended in 7 ml THF and brought to -5 ºC. A canula was used to transfer the solution of starting material to the NaH. After 45 min, NaI (25 mg, 0.17 mmol, 0.1 eq.) and (E)-ethyl 4-bromo-2-methylbut-2-enoate **(3.23)** (584 mg, 2.03 mmol, 1.2 eq.) were added. The reaction mixture was covered with foil and stirred overnight for 15 h, then brought to 0 ºC and quenched with 1M NaOH. Aqueous separation with EtOAc (x3) was followed by drying of the combined organic layers with Na_2SO_4 and concentration *in vacuo*. Column chromatography (SiO_2; 30% EtOAc/Hex) afforded **3.24** (310 mg, 53% yield) as a light yellow oil. ^{1}H-NMR (500 MHz, C_6D_6) δ 6.91 (tq, *J* = 1.5, 7.3, 1H), 6.84 (t, *J* = 8.3, 1H), 6.37 (d, *J* = 8.3, 1H), 6.21 (d, *J* = 8.3, 1H), 4.72 (s, 2H), 3.86 (q, *J* = 7.1, 2H), 3.02 (s, 3H), 2.71 (ddd, *J* = 1.0, 7.3, 15.6, 1H), 2.43 – 2.32 (m, 1H), 1.67 (d, *J* = 1.0, 3H), 0.85 (t, *J* = 7.1, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 188.28, 171.51, 166.44, 156.87, 140.73, 134.37, 129.87, 114.82, 108.50, 108.35, 105.85, 94.58, 80.43, 60.67, 56.24, 34.92, 14.02, 12.89; FTIR (thin film/KCl) FTIR (thin film/KCl) 2980, 2939, 2830, 1713, 1614, 1490, 1443, 1329, 1258, 1157, 1097, 1054, 1014, 924, 872, 800, 774 cm^{-1}; HRMS (EI) *m/z* found 345.1208 [calc'd for $C_{18}H_{19}O_6N$: 345.1212].



(E)-Ethyl 4-(2-cyano-4-hydroxy-3-oxo-2,3-dihydrobenzofuran-2-yl)-2-methylbut-2-enoate (3.25a): In a flask with magnetic stirring was dissolved **3.24** (30.9 mg, 0.0895 mmol) in 1 ml of a 5% (v/v) HCl/EtOH solution. The reaction was stirred at ambient temperature overnight for 17h, then at 40 ^{o}C for 5 h. The reaction mixture was diluted with $H_2O$and brine and separated with EtOAc (x3). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 3% MeOH/DCM) provided the free phenol **3.25a** (17.4 mg, 64% yield) as a yellow solid. ^{1}H-NMR (300 MHz, C_6D_6) δ 6.86 (td, *J* = 1.3, 7.5, 1H), 6.78 (d, *J* = 8.2, 1H), 6.19 (d, *J* = 8.3, 1H), 6.06 (d, *J* = 8.2, 1H), 3.88 (q, *J* = 7.2, 2H),

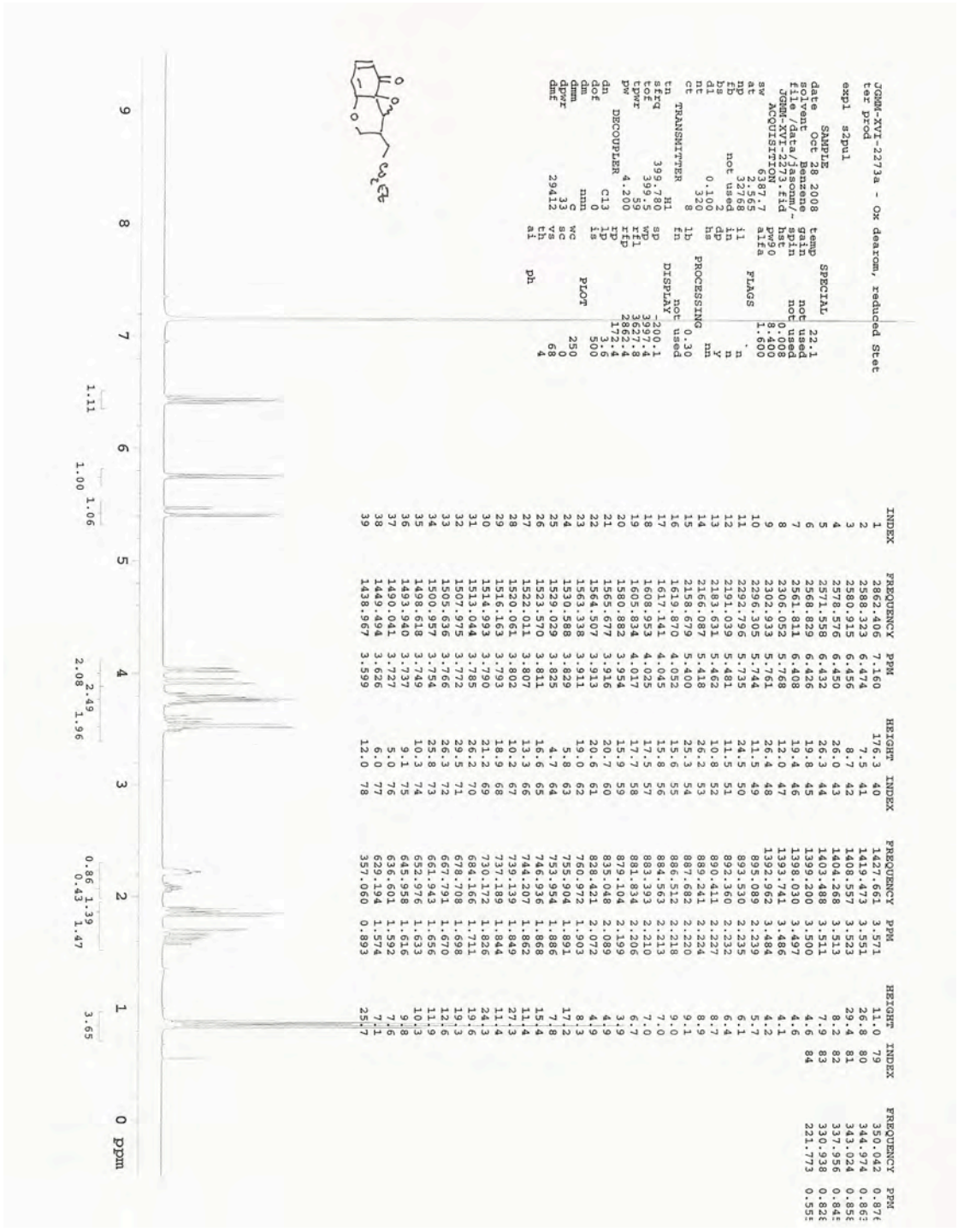
2.62 (dd, J = 7.5, 15.6, 1H), 2.28 (dd, J = 7.4, 15.6, 1H), 1.67 (d, J = 0.6, 3H), 0.87 (t, J = 7.2, 3H); ^{13}C-NMR (75 MHz, C_6D_6) δ 191.98, 169.68, 166.64, 157.34, 142.02, 134.54, 129.64, 114.16, 110.20, 106.46, 104.04, 80.31, 60.91, 34.64, 14.0, 12.9; FTIR (thin film/KCl) 3296, 2986, 2940, 2906, 1717, 1621, 1494, 1461, 1371, 1309, 1250, 1197, 1147, 1053, 1010, 920, 867, 777 cm^{-1}; HRMS (EI) *m/z* found 301.0945 [calc'd for $C_{16}H_{15}O_5N$: 301.0950].



Major (desired) Minor (undesired)

(E)-ethyl 4-(2-cyano-3,4-dihydroxy-2,3-dihydrobenzofuran-2-yl)-2-methylbut-2-enoate (3.25): In a flask with magnetic stirring was dissolved **3.25a** (7.5 mg, 0.025 mmol, 1.0 eq.) in MeOH at 0 ºC. $NaBH_4$ (1.9 mg, 0.050 mmol, 2.0 eq.) was added and the reaction mixture became yellow. After stirring for 30 min another 1.9 mg portion of $NaBH_4$ was added. The reaction was quenched with 20 wt% Rochelle salt and stirred at 0 ºC overnight. Aqueous separation with EtOAc (x3) and drying of the combined organic layers with Na_2SO_4 was followed by concentration *in vacuo*. Column chromatography (SiO_2; 3% MeOH/DCM) provided the diol (7.2 mg, 96% yield) as a 2:1 mixture of desired:undesired diastereomers (determined by NOESY1D). **Major diastereomer:** ^{1}H-NMR (500 MHz, C_6D_6) δ 6.95 (td, J = 1.5, 7.4, 1H), 6.86 (t, J = 8.1, 1H), 6.40 (d, J = 8.3, 2H), 6.30 (d, J = 8.1, 1H), 5.04 (s, 1H), 3.97 – 3.81 (m, 2H), 2.40 (dd, J = 7.6, 15.1, 1H), 2.19 (dd, J = 7.2, 15.3, 1H), 1.66 (d, J = 0.5, 3H), 0.90 (q, J = 7.1, 3H); ^{13}C-NMR (determined by HSQC, HMBC) δ 167.8, 159.0, 154.9, 133.6, 132.6, 131.7, 116.1, 112.2, 110.3, 103.3, 87.8, 76.4, 61.1, 36.0, 14.1, 12.8. **Minor diastereomer:** ^{1}H-NMR (500 MHz, C_6D_6) δ 7.11 (td, J = 1.4, 7.4, 1H), 6.89 (t, J = 8.1, 1H), 6.44 (d, J = 8.2, 1H), 6.40 (d, J = 8.2, 1H), 5.53 (s, 1H), 3.97 – 3.79 (m, 2H), 3.26 (dt, J = 6.9, 21.1, 1H), 2.92 – 2.71 (m, 2H), 1.76 (s, 3H), 0.90 (q, J = 7.1, 3H); ^{13}C-NMR (determined by HSQC, HMBC) δ 168.8, 159.5, 154.6, 133.7, 132.8, 132.6, 119.0, 110.0, 103.3, 85.0, 74.8, 61.1, 31.9, 14.1, 12.7 HRMS (EI) *m/z* found 219.0529 [calc'd for $C_{11}H_9O_4N$: 219.0532]. FTIR (thin film/KCl) 3378, 2984, 2938, 1691, 1621, 1467, 1371, 1305, 1277, 1240, 914, 863, 738 cm^{-1}; HRMS (EI) *m/z* found 303.1101 [calc'd for $C_{16}H_{17}O_5N$: 303.1107].

A3.2 ^{1}H and ^{13}C NMR Spectra



JGMM-XVI-2273C - Carbon of ox dearom. of reduced Stetter prod

expl s2pul

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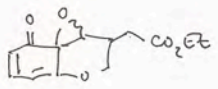
tpwr	53	lb	0.50
pw	6.0	wtfile	
dl	1.500	proc	ft
tof	1255.5	fn	not used
nt	3200	math	f
ct	512		
alock	n	werr	
gain	not used	wexp	wft
FLAGS		wbs	wft
il	n	wnt	
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1238.6		
wp	28890.9		
vs	832		
sc	0		
wc	250		
hzmm	115.56		
is	500.00		
rfl	17329.2		
rfp	16090.1		
th	5		
ins	100.000		
nm cdc ph			

INDEX	FREQUENCY	PPM	HEIGHT
1	23945.584	190.491	8.5
2	23939.853	190.446	13.6
3	21399.698	170.238	17.5
4	21376.333	170.053	11.4
5	20060.407	159.584	13.2
6	20050.267	159.503	8.9
7	18136.554	144.280	43.7
8	18129.060	144.220	20.5
9	16125.854	128.284	64.7
10	16113.511	128.186	793.2
11	16102.049	128.095	28.0
12	16089.264	127.993	822.6
13	16077.802	127.902	33.0
14	16065.018	127.800	832.4
15	14918.377	118.678	60.7
16	14908.237	118.598	26.8
17	12971.600	103.191	25.9
18	12935.010	102.900	63.9
19	8258.072	65.694	25.8
20	8229.417	65.466	62.3
21	7903.632	62.875	60.9
22	7885.998	62.735	27.7
23	7623.695	60.648	19.2
24	7616.200	60.588	43.8
25	6835.021	54.374	6.7
26	6738.035	53.602	16.5
27	4125.139	32.816	20.9
28	3973.929	31.613	19.9
29	3970.843	31.589	43.8
30	3967.316	31.561	49.0
31	1762.644	14.022	19.8
32	1756.913	13.977	44.8



JGMM-VIII-1091 - DIBAL-H red. of Stetter prod. to ald

expl s2pul

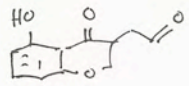
SAMPLE		SPECIAL	
date	May 25 2006	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/-JasonMBook8/JGMM-V-III-1091.fid	spin	20
		hst	0.008
		pw90	8.400
ACQUISITION		alfa	1.600
sw	6387.7	FLAGS	
at	3.000	il	n
np	38326	in	n
fb	not used	dp	y
bs	2	hs	nn
d1	1.000	PROCESSING	
nt	32	lb	0.30
ct	12	fn	not used
TRANSMITTER		DISPLAY	
tn	H1	sp	-765.2
sfrq	399.780	wp	6387.5
tof	399.5	rfl	3627.8
tpwr	58	rfp	2862.4
pw	4.200	rp	-88.3
DECOUPLER		lp	3.7
dn	C13	is	500
dof	0	PLOT	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	33	vs	422
dmf	29412	th	8
		ai ph	

INDEX	FREQUENCY	PPM	HEIGHT
1	4820.950	12.059	79.2
2	3599.467	9.004	60.1
3	2862.406	7.160	1077.9
4	2781.896	6.959	8.6
5	2760.648	6.905	21.6
6	2752.266	6.884	45.1
7	2744.078	6.864	25.4
8	2602.358	6.510	34.5
9	2593.976	6.489	31.3
10	2512.102	6.284	33.9
11	2503.915	6.263	31.8
12	1491.210	3.730	23.4
13	1485.752	3.716	24.3
14	1480.099	3.702	27.6
15	1474.641	3.689	27.9
16	1357.873	3.397	25.6
17	1346.176	3.367	39.1
18	1334.870	3.339	23.6
19	1098.215	2.747	11.5
20	1093.147	2.734	8.5
21	1091.002	2.729	14.5
22	1086.129	2.717	13.7
23	1084.374	2.712	8.3
24	1078.916	2.699	10.9
25	852.593	2.133	17.7
26	847.524	2.120	17.2
27	834.074	2.086	20.3
28	829.005	2.074	19.5
29	585.333	1.464	21.1
30	577.925	1.446	20.8
31	566.813	1.418	18.7
32	559.406	1.399	18.3
33	158.418	0.396	70.7

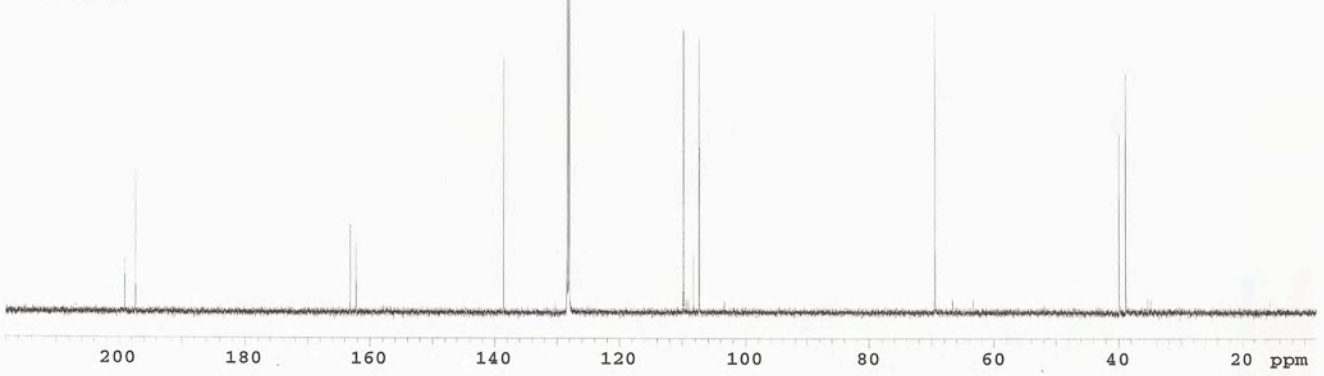
JDF-II-42C - Carbon of R4 aldehyde

exp1 s2pul

SAMPLE		DEC. & VT	
date	Oct 28 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/-	dpwr	40
	JDF-II-42C.fid	dof	0
ACQUISITION		dm	yyy
sfrq	125.717	dmm	w
tn	C13	dmf	13333
at	1.300	dseq	
np	75146	dres	1.0
sw	28891.3	homo	n
fb	16000	temp	20.0
bs	4	PROCESSING	
tpwr	53	lb	0.50
pw	6.0	wtfile	
d1	1.500	proc	ft
tof	1255.5	fn	not used
nt	3200	math	f
ct	40		
alock	n	werr	
gain	not used	wexp	wft
FLAGS		wbs	wft
il	n	wnt	
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	1025.1		
wp	26385.1		
vs	136		
sc	0		
wc	250		
hzmm	105.54		
is	500.00		
rfl	17305.0		
rfp	16090.1		
th	7		
ins	100.000		
nm cdc ph			



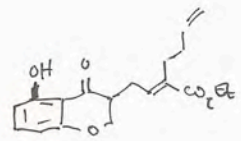
INDEX	FREQUENCY	PPM	HEIGHT
1	25023.009	199.063	10.1
2	24813.607	197.397	26.5
3	20510.949	163.168	16.5
4	20387.071	162.183	12.9
5	17419.294	138.574	48.1
6	16150.980	128.484	10.1
7	16138.636	128.386	130.3
8	16114.389	128.193	134.3
9	16090.143	128.000	135.9
10	13805.237	109.823	53.8
11	13610.824	108.277	11.0
12	13502.376	107.414	52.1
13	8733.301	69.475	57.1
14	5016.086	39.904	33.9
15	4882.510	38.841	45.1



JGMM-VIII-1110b2 - Later NMR of HWE, R4, E only

expl s2pul

SAMPLE		SPECIAL	
date	Oct 27 2008	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/-	spin	20
JGMM-VIII-1110b2.f-		hst	0.008
	id	pw90	14.000
ACQUISITION		alfa	-6.900
sw	4789.3	FLAGS	
at	3.000	il	n
np	28736	in	n
fb	not used	dp	y
bs	2	hs	nn
ss	2	PROCESSING	
d1	1.000	lb	0.30
nt	320	fn	65536
ct	4	DISPLAY	
TRANSMITTER		sp	-142.2
tn	H1	wp	4191.2
sfrq	299.763	rfl	2729.0
tof	265.1	rfp	2146.3
tpwr	58	rp	126.0
pw	5.600	lp	-4.2
DECOUPLER		PLOT	
dn	C13	wc	250
dof	0	sc	0
dm	nnn	vs	209
dmm	c	th	7
dpwr	46	ai ph	
dmf	13100		



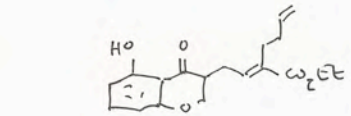
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3640.223	12.144	89.1	40	715.622	2.387	17.3
2	2146.353	7.160	23.0	41	712.407	2.377	24.3
3	2091.106	6.976	24.1	42	708.168	2.362	37.9
4	2082.775	6.948	52.0	43	705.245	2.353	34.9
5	2074.590	6.921	29.3	44	698.960	2.332	35.1
6	2006.481	6.694	17.3	45	659.498	2.200	18.8
7	1999.611	6.671	21.2	46	657.890	2.195	18.4
8	1998.004	6.665	22.2	47	652.775	2.178	44.1
9	1991.280	6.643	18.2	48	648.536	2.164	29.9
10	1951.233	6.509	40.8	49	644.298	2.149	39.1
11	1942.902	6.482	36.0	50	639.328	2.133	19.9
12	1888.094	6.299	40.1	51	634.797	2.118	8.9
13	1879.909	6.271	36.9	52	602.789	2.011	13.5
14	1735.067	5.788	10.0	53	594.166	1.982	22.3
15	1724.836	5.754	16.4	54	587.735	1.961	12.2
16	1717.967	5.731	16.9	55	585.689	1.954	11.6
17	1707.882	5.697	12.9	56	579.112	1.932	18.0
18	1509.693	5.036	20.9	57	570.488	1.903	8.0
19	1508.232	5.031	22.5	58	308.867	1.030	75.3
20	1492.593	4.979	18.6	59	301.706	1.006	151.2
21	1491.131	4.974	20.3	60	294.544	0.983	73.4
22	1483.969	4.951	22.4	61	289.575	0.966	8.6
23	1482.800	4.947	21.1	62	281.974	0.941	9.4
24	1473.885	4.917	20.3				
25	1472.715	4.913	19.0				
26	1218.987	4.067	24.3				
27	1211.825	4.043	73.3				
28	1204.810	4.019	74.3				
29	1197.648	3.995	25.0				
30	1131.000	3.773	20.4				
31	1126.177	3.757	21.7				
32	1119.600	3.735	27.0				
33	1114.777	3.719	27.1				
34	1051.929	3.509	25.9				
35	1042.575	3.478	28.4				
36	1040.529	3.471	22.7				
37	1031.175	3.440	20.9				
38	723.515	2.414	9.0				
39	718.399	2.397	13.2				

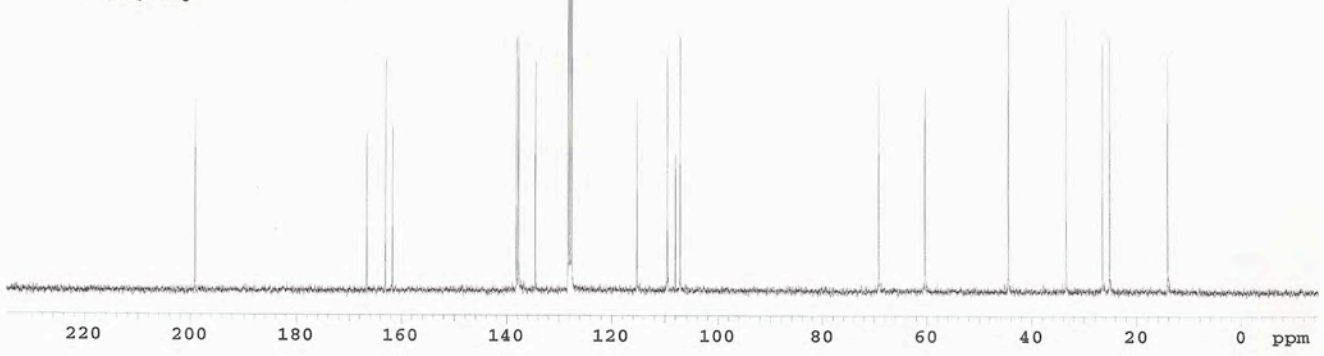
JGMM-VIII-1110bC - Carbon of R4 HWE, E isomer only

expl s2pul

SAMPLE		SPECIAL	
date	Oct 27 2008	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/-	spin	20
JGMM-VIII-1110bC.f-	id	hst	0.008
		pw90	14.000
ACQUISITION		alfa	-8.800
sw	18797.0	FLAGS	
at	2.500	il	n
np	93984	in	n
fb	not used	dp	y
bs	4	hs	nn
d1	2.000	PROCESSING	
nt	3200	lb	1.00
ct	80	fn	131072
TRANSMITTER		DISPLAY	
tn	C13	sp	-1107.0
sfrq	75.383	wp	18796.7
tof	727.6	rfl	1107.2
tpwr	59	rfp	0
pw	6.000	rp	123.7
DECOUPLER		lp	5.5
dn	H1	PLOT	
dof	0	wc	250
dm	yyy	sc	0
dmm	w	vs	160
dpwr	36	th	16
dmf	7700	ai	ph

INDEX	FREQUENCY	PPM	HEIGHT
1	15011.141	199.153	35.6
2	12559.696	166.629	29.4
3	12290.086	163.053	43.6
4	12188.839	161.709	30.8
5	10416.869	138.201	47.7
6	10389.908	137.843	48.2
7	10387.900	137.816	47.7
8	10138.081	134.502	43.4
9	9664.542	128.219	152.3
10	9640.162	127.896	152.8
11	9616.069	127.576	152.2
12	8687.348	115.255	36.6
13	8257.980	109.559	44.4
14	8138.663	107.976	25.6
15	8068.966	107.051	48.1
16	5212.245	69.151	38.8
17	4551.700	60.387	38.4
18	3354.230	44.501	53.9
19	2521.880	33.458	51.7
20	1997.000	26.494	46.9
21	1890.017	25.075	47.8
22	1067.706	14.165	44.4



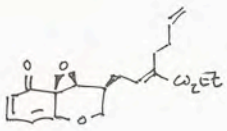


JGMM-Char2 - R4 full quinol, upper spot

expl s2pul

SAMPLE		SPECIAL	
date	Nov 13 2008	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/~	spin	20
	JGMM-Char2-R4q_upp~	hst	0.008
	er.fid	pw90	7.600
ACQUISITION		alfa	1.600
sw	6387.7	FLAGS	
at	2.565	il	n
np	32768	in	n
fb	not used	dp	y
bs	2	hs	nn
dl	3.000	PROCESSING	
nt	320	lb	0.30
ct	8	fn	not used
TRANSMITTER		DISPLAY	
tn	H1	sp	-200.1
sfrq	399.780	wp	3997.4
tof	399.5	rfl	3627.4
tpwr	59	rfp	2862.4
pw	4.200	rp	173.5
DECOUPLER		lp	0.2
dn	C13	is	500
dof	0	PLOT	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	33	vs	78
dmf	29412	th	8
		ai ph	

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2862.406	7.160	227.0	40	881.444	2.205	11.9
2	2631.989	6.584	12.1	41	874.426	2.187	21.1
3	2624.581	6.565	22.9	42	867.018	2.169	16.2
4	2616.784	6.546	11.9	43	714.967	1.788	10.4
5	2598.070	6.499	15.6	44	707.559	1.770	12.9
6	2591.052	6.481	17.2	45	699.761	1.750	14.0
7	2588.323	6.474	17.2	46	692.354	1.732	8.1
8	2581.305	6.457	17.7	47	619.057	1.549	14.5
9	2318.528	5.800	26.6	48	611.649	1.530	10.8
10	2308.392	5.774	24.6	49	603.852	1.510	10.6
11	2294.356	5.739	10.4	50	534.064	1.336	9.0
12	2287.728	5.723	11.0	51	528.995	1.323	12.2
13	2277.591	5.697	8.1	52	522.368	1.307	11.2
14	2198.836	5.500	26.3	53	517.299	1.294	8.0
15	2191.818	5.483	24.3	54	404.625	1.012	49.0
16	2029.630	5.077	13.4	55	397.607	0.995	97.0
17	2028.070	5.073	14.8	56	390.589	0.977	46.6
18	2012.475	5.034	12.2	57	194.871	0.487	15.7
19	2010.916	5.030	13.5				
20	2004.288	5.014	15.7				
21	2003.508	5.012	14.8				
22	1994.151	4.988	14.2				
23	1993.371	4.986	13.2				
24	1625.718	4.067	15.5				
25	1618.700	4.049	47.3				
26	1611.682	4.031	48.2				
27	1604.665	4.014	16.9				
28	1495.109	3.740	37.4				
29	1463.919	3.662	12.7				
30	1452.613	3.634	21.1				
31	1441.306	3.605	15.2				
32	1326.683	3.319	11.1				
33	1321.614	3.306	11.2				
34	1316.156	3.292	9.5				
35	1311.088	3.280	9.3				
36	930.568	2.328	8.4				
37	922.771	2.308	24.9				
38	915.363	2.290	24.5				
39	909.515	2.275	15.1				

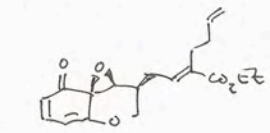


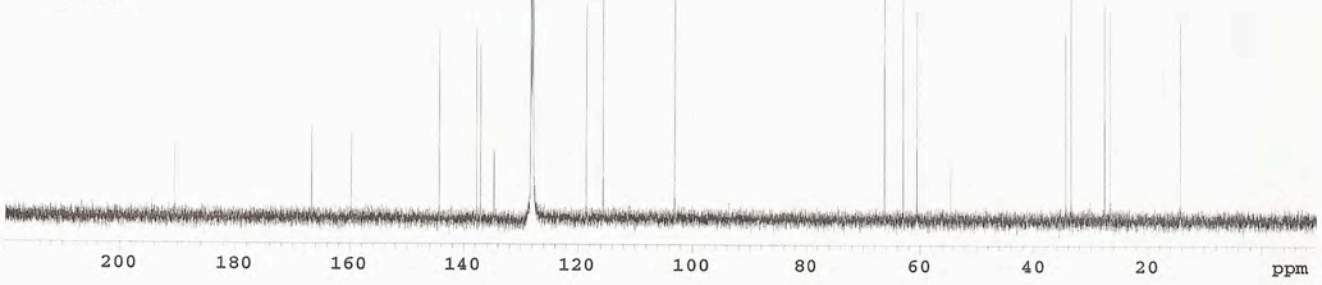
JGMM-Char2-R4q_upperC

expl s2pul

SAMPLE		DEC. & VT	
date	Nov 14 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/-JGMM-Char2-R4q_upp-erC.fid	dpwr	40
		dof	0
		dm	yyy
ACQUISITION		dmm	w
sfrq	125.717	dmf	13333
tn	C13	dseq	
at	1.300	dres	1.0
np	75146	homo	n
sw	28891.3	PROCESSING	
fb	16000	lb	0.50
bs	4	wtfile	
tpwr	53	proc	ft
pw	6.0	fn	not used
d1	1.500	math	f
tof	1255.5		
nt	1000	werr	
ct	636	wexp	wft
alock	n	wbs	wft
gain	not used	wnt	
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1237.3		
wp	28890.9		
vs	1138		
sc	0		
wc	250		
hzmm	115.56		
is	500.00		
rfl	17327.9		
rfp	16090.1		
th	8		
ins	100.000		
nm cdc ph			

INDEX	FREQUENCY	PPM	HEIGHT
1	23954.842	190.565	13.8
2	20952.238	166.679	17.2
3	20088.621	159.809	16.0
4	18134.790	144.266	35.2
5	17316.580	137.757	36.2
6	17229.292	137.062	33.0
7	16928.194	134.667	12.8
8	16126.295	128.288	63.3
9	16113.951	128.189	1078.3
10	16102.049	128.095	32.6
11	16089.705	127.996	1121.7
12	16077.802	127.902	39.8
13	16065.458	127.804	1137.9
14	14904.269	118.566	40.6
15	14530.432	115.592	44.9
16	12949.998	103.020	44.4
17	8327.285	66.245	42.7
18	7916.857	62.980	47.8
19	7608.265	60.525	39.3
20	6855.300	54.535	10.2
21	4330.133	34.447	35.4
22	4212.867	33.514	45.0
23	3470.923	27.612	40.9
24	3341.315	26.581	39.7
25	1789.977	14.240	37.6



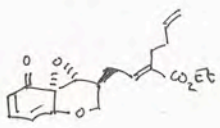


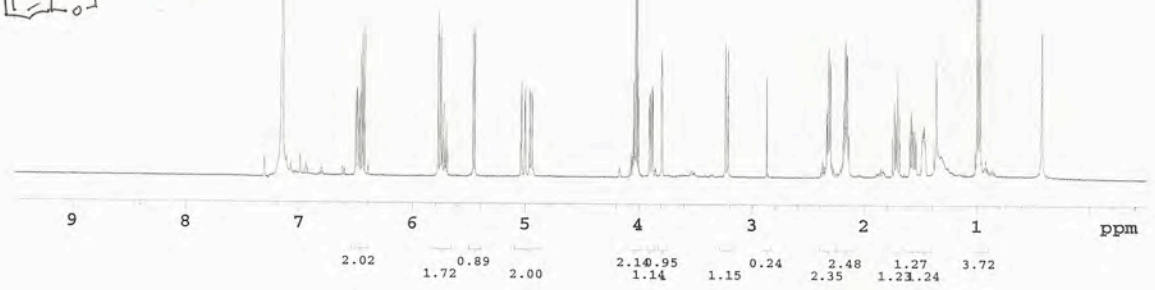
JGMM-Char2-R4q_lower2

expl s2pul

SAMPLE		DEC. & VT	
date	Nov 14 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
JGMM-Char-R4q_lowe~	r.fid	dof	0
ACQUISITION		dm	nnn
		dmm	c
sfrq	499.920	dmf	200
tn	H1	dseq	
at	1.892	dres	1.0
np	30272	homo	n
sw	8000.0	**PROCESSING**	
fb	4000	wtfile	
bs	2	proc	ft
tpwr	58	fn	not used
pw	5.5	math	f
d1	2.000		
tof	0	werr	
nt	320	wexp	wft
ct	10	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	645		
sc	35		
wc	215		
hzmm	23.22		
is	33.57		
rfl	5073.2		
rfp	3579.4		
th	7		
ins	2.000		
nm	ph		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM
1	3579.408	7.160	645.4	40	1896.302	3.793	23.6			
2	3253.236	6.508	14.5	41	1894.837	3.790	21.1			
3	3246.400	6.494	16.5	42	1619.935	3.240	25.4			
4	3244.447	6.490	16.8	43	1608.705	3.218	24.3			
5	3237.611	6.476	14.7	44	1436.830	2.874	19.1			
6	3230.775	6.463	23.5	45	1167.787	2.336	12.5			
7	3223.451	6.448	27.8	46	1164.857	2.330	13.6			
8	3221.009	6.443	23.8	47	1160.462	2.321	24.5			
9	3213.685	6.428	28.9	48	1158.021	2.316	25.2			
10	2887.025	5.775	31.4	49	1150.697	2.302	22.0			
11	2879.701	5.760	9.8	50	1151.673	2.304	22.0			
12	2877.259	5.755	28.6	51	1091.615	2.184	14.3			
13	2869.447	5.740	13.3	52	1084.779	2.170	26.4			
14	2862.611	5.726	13.9	53	1076.478	2.153	23.6			
15	2852.357	5.706	10.4	54	1068.666	2.138	8.2			
16	2733.216	5.467	28.2	55	1070.130	2.141	8.3			
17	2725.892	5.453	28.1	56	877.259	1.755	8.1			
18	2519.349	5.040	15.3	57	867.982	1.736	14.3			
19	2517.396	5.036	18.4	58	862.611	1.726	11.2			
20	2515.931	5.033	7.9	59	859.193	1.719	9.4			
21	2502.259	5.005	14.6	60	853.334	1.707	20.5			
22	2500.306	5.001	16.9	61	844.056	1.688	12.2			
23	2498.841	4.999	7.4	62	799.134	1.599	8.3			
24	2481.752	4.964	16.6	63	793.275	1.587	12.8			
25	2480.775	4.962	15.1	64	786.927	1.574	10.4			
26	2479.798	4.960	15.9	65	778.627	1.558	9.0			
27	2471.498	4.944	16.1	66	772.279	1.545	7.5			
28	2470.521	4.942	14.2	67	743.959	1.488	8.6			
29	2469.544	4.940	15.1	68	741.517	1.483	8.3			
30	2022.279	4.045	18.1	69	738.587	1.477	10.0			
31	2015.443	4.032	56.5	70	735.658	1.472	10.0			
32	2008.119	4.017	56.9	71	733.216	1.467	7.3			
33	2001.283	4.003	20.5	72	680.970	1.362	22.2			
34	1951.966	3.905	15.8	73	500.306	1.001	15.4			
35	1949.037	3.899	16.0	74	498.841	0.998	79.3			
36	1940.736	3.882	17.4	75	491.517	0.983	153.4			
37	1937.806	3.876	17.5	76	487.123	0.974	8.2			
38	1898.744	3.798	20.4	77	484.681	0.970	69.6			
39	1897.279	3.795	23.8	78	210.755	0.422	30.0			



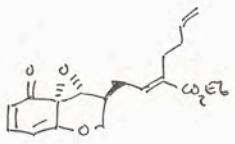


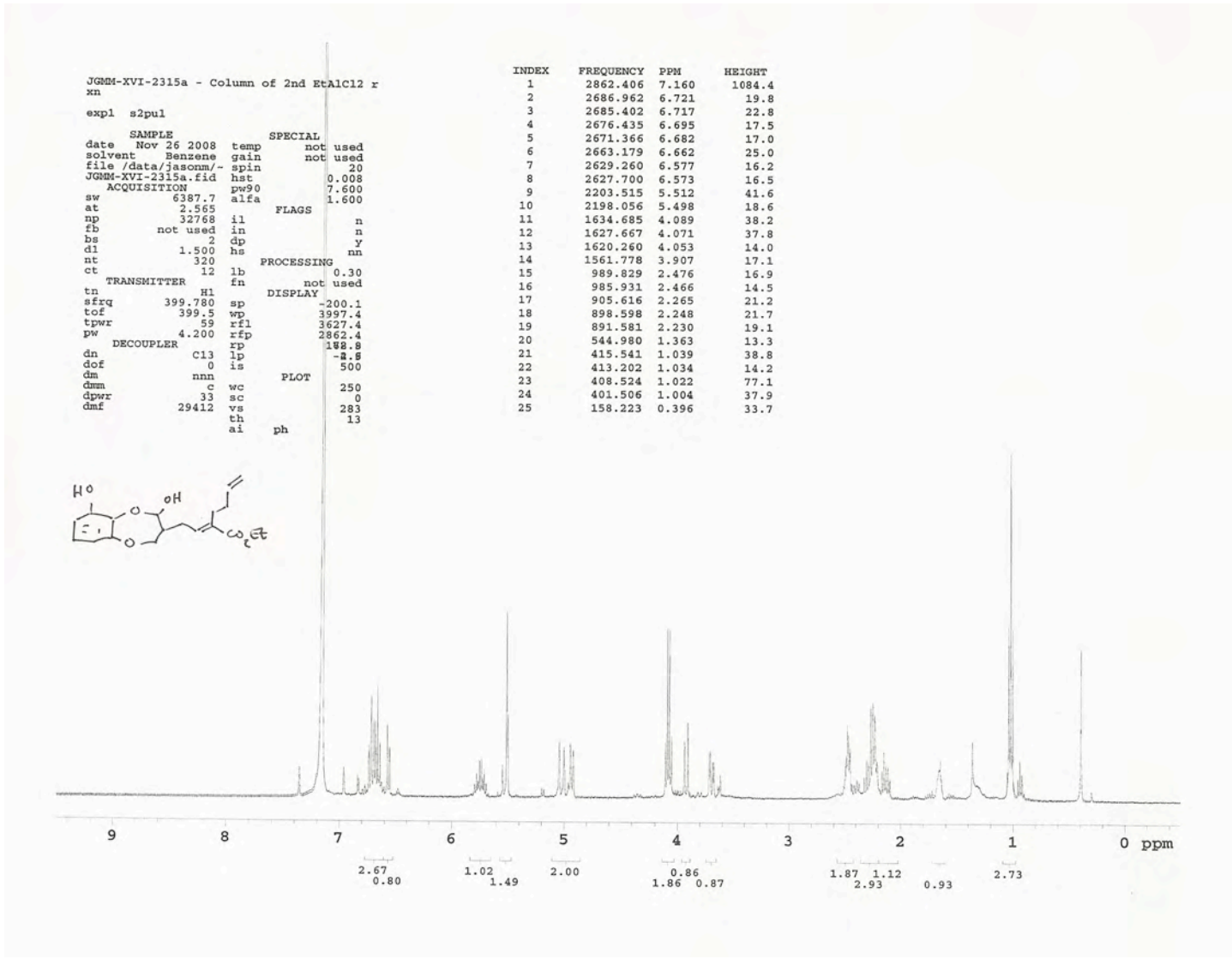
JGMM-Char2-R4q_lowerC - R4 spiroquinol, lower diastereomer

exp1 s2pul

SAMPLE		DEC. & VT	
date	Nov 16 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	40
JGMM-Char2-R4q_low~	erC2.fid	dof	0
ACQUISITION		dm	YYY
		dmm	w
sfrq	125.717	dmf	13333
tn	C13	dseq	
at	1.300	dres	1.0
np	75146	homo	n
sw	28891.3	PROCESSING	
fb	16000	lb	0.50
bs	4	wtfile	
tpwr	53	proc	ft
pw	6.0	fn	not used
dl	1.500	math	f
tof	1255.5		
nt	32000	werr	
ct	2268	wexp	wft
alock	n	wbs	wft
gain	not used	wnt	
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1236.9		
wp	28890.9		
vs	2732		
sc	0		
wc	250		
hzmm	115.56		
is	500.00		
rfl	17327.5		
rfp	16090.1		
th	5		
ins	100.000		
nm cdc ph			

INDEX	FREQUENCY	PPM	HEIGHT
1	23948.670	190.516	7.8
2	20952.679	166.682	11.0
3	20097.438	159.879	13.2
4	18148.457	144.374	23.6
5	17330.687	137.869	27.3
6	17265.442	137.350	21.0
7	16951.118	134.849	9.3
8	16126.736	128.291	169.7
9	16114.392	128.193	2605.9
10	16102.489	128.098	89.9
11	16090.146	128.000	2701.5
12	16078.243	127.905	107.0
13	16065.899	127.807	2732.4
14	16024.900	127.481	9.0
15	14921.903	118.706	41.2
16	14500.013	115.350	35.8
17	12915.612	102.746	41.5
18	8165.494	64.958	30.0
19	7986.511	63.534	33.9
20	7605.620	60.504	31.9
21	6780.797	53.942	9.7
22	4335.423	34.489	32.2
23	4221.243	33.581	37.2
24	3791.859	30.165	7.7
25	3334.261	26.525	38.2
26	3313.541	26.360	30.2
27	1790.418	14.243	33.9



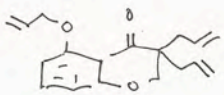

JGMM-XVI-2315a - Column of 2nd EtAlCl2 r
xn
expl s2pul
SAMPLE
date Nov 26 2008
solvent Benzene
file /data/jasonm/-
JGMM-XVI-2315a.fid
ACQUISITION
sw 6387.7
at 2.565
np 32768
fb not used
bs 2
d1 1.500
nt 320
ct 12
TRANSMITTER
tn H1
sfrq 399.780
tof 399.5
tpwr 59
pw 4.200
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 33
dmf 29412
SPECIAL
temp not used
gain not used
spin 20
hst 0.008
pw90 7.600
alfa 1.600
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.30
fn not used
DISPLAY
sp -200.1
wp 3997.4
rfl 3627.4
rfp 2862.4
rp 1[illegible]
lp -[illegible]
is 500
PLOT
wc 250
sc 0
vs 283
th 13
ai ph
INDEX FREQUENCY PPM HEIGHT
1 2862.406 7.160 1084.4
2 2686.962 6.721 19.8
3 2685.402 6.717 22.8
4 2676.435 6.695 17.5
5 2671.366 6.682 17.0
6 2663.179 6.662 25.0
7 2629.260 6.577 16.2
8 2627.700 6.573 16.5
9 2203.515 5.512 41.6
10 2198.056 5.498 18.6
11 1634.685 4.089 38.2
12 1627.667 4.071 37.8
13 1620.260 4.053 14.0
14 1561.778 3.907 17.1
15 989.829 2.476 16.9
16 985.931 2.466 14.5
17 905.616 2.265 21.2
18 898.598 2.248 21.7
19 891.581 2.230 19.1
20 544.980 1.363 13.3
21 415.541 1.039 38.8
22 413.202 1.034 14.2
23 408.524 1.022 77.1
24 401.506 1.004 37.9
25 158.223 0.396 33.7
HO
OH
CO2Et
9
8
7
6
5
4
3
2
1
0 ppm
2.67
0.80
1.02
1.49
2.00
0.86
1.86
0.87
1.87
2.93
1.12
0.93
2.73

JGMM-Char2-R4triallyl

expl s2pul

SAMPLE		SPECIAL	
date	Nov 18 2008	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/-JGMM-Char2-R4trial-lyl.fid	spin	20
		hst	0.008
		pw90	14.000
		alfa	-6.900
ACQUISITION		FLAGS	
sw	4789.3	il	n
at	3.000	in	n
np	28736	dp	y
fb	not used	hs	nn
bs	2	PROCESSING	
ss	2	lb	0.30
d1	1.000	fn	65536
nt	320	DISPLAY	
ct	4	sp	-149.9
TRANSMITTER		wp	2997.5
tn	H1	rf1	2729.1
sfrq	299.763	rfp	2146.3
tof	265.1	rp	127.3
tpwr	58	lp	-7.1
pw	5.600	PLOT	
DECOUPLER		wc	250
dn	C13	sc	0
dof	0	vs	153
dm	nnn	th	9
dmm	c	ai ph	
dpwr	46		
dmf	13100		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2146.499	7.161	71.5	40	665.052	2.219	18.5
2	2094.029	6.986	19.7	41	657.598	2.194	17.3
3	2085.698	6.958	42.2				
4	2077.513	6.931	23.6				
5	1977.834	6.598	29.9				
6	1969.503	6.570	25.7				
7	1831.677	6.110	29.0				
8	1823.346	6.083	27.4				
9	1754.068	5.852	13.4				
10	1752.314	5.846	54.6				
11	1747.198	5.829	51.0				
12	1745.298	5.822	24.2				
13	1742.521	5.813	10.5				
14	1729.221	5.769	18.3				
15	1721.621	5.743	13.8				
16	1720.013	5.738	14.2				
17	1717.090	5.728	10.0				
18	1714.167	5.718	10.0				
19	1711.390	5.709	15.3				
20	1709.490	5.703	15.1				
21	1702.036	5.678	22.1				
22	1694.728	5.654	10.8				
23	1557.779	5.197	13.0				
24	1555.733	5.190	11.1				
25	1552.225	5.178	13.2				
26	1550.617	5.173	20.4				
27	1545.209	5.155	11.3				
28	1475.639	4.923	92.3				
29	1463.800	4.883	39.0				
30	1460.146	4.871	34.5				
31	1246.757	4.159	41.2				
32	1244.564	4.152	74.3				
33	1182.448	3.945	151.4				
34	733.307	2.446	17.6				
35	725.999	2.422	17.3				
36	719.276	2.399	29.3				
37	711.822	2.375	27.9				
38	679.229	2.266	30.0				
39	671.629	2.241	29.2				

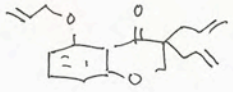


JGMM-Char2-R4triallylC

expl s2pul

SAMPLE		SPECIAL	
date	Nov 18 2008	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/~	spin	20
	JGMM-Char2-R5trial~	hst	0.008
	lylC.fid	pw90	14.000
ACQUISITION		alfa	-8.800
sw	18797.0	FLAGS	
at	2.500	il	n
np	93984	in	n
fb	not used	dp	y
bs	4	hs	nn
d1	1.000	PROCESSING	
nt	2560	lb	1.00
ct	88	fn	131072
TRANSMITTER		DISPLAY	
tn	C13	sp	-1107.0
sfrq	75.383	wp	18796.7
tof	727.6	rf1	1107.2
tpwr	59	rfp	0
pw	6.000	rp	114.0
DECOUPLER		lp	17.2
dn	H1	PLOT	
dof	0	wc	250
dm	yyy	sc	0
dmm	w	vs	162
dpwr	36	th	8
dmf	7700	ai	ph

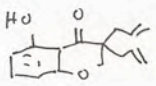
INDEX	FREQUENCY	PPM	HEIGHT
1	14978.731	198.723	14.4
2	13040.119	173.003	16.6
3	11856.702	157.303	17.4
4	10465.628	138.847	40.6
5	9981.764	132.428	31.9
6	9880.230	131.081	58.7
7	9681.464	128.444	13.6
8	9665.402	128.231	117.0
9	9641.310	127.911	117.7
10	9616.930	127.588	117.0
11	9007.439	119.502	57.5
12	8840.510	117.287	31.0
13	8407.413	111.541	10.6
14	7914.657	105.004	34.7
15	7869.053	104.399	38.0
16	6849.697	90.875	28.8
17	5203.354	69.033	37.4
18	3039.876	40.330	77.8



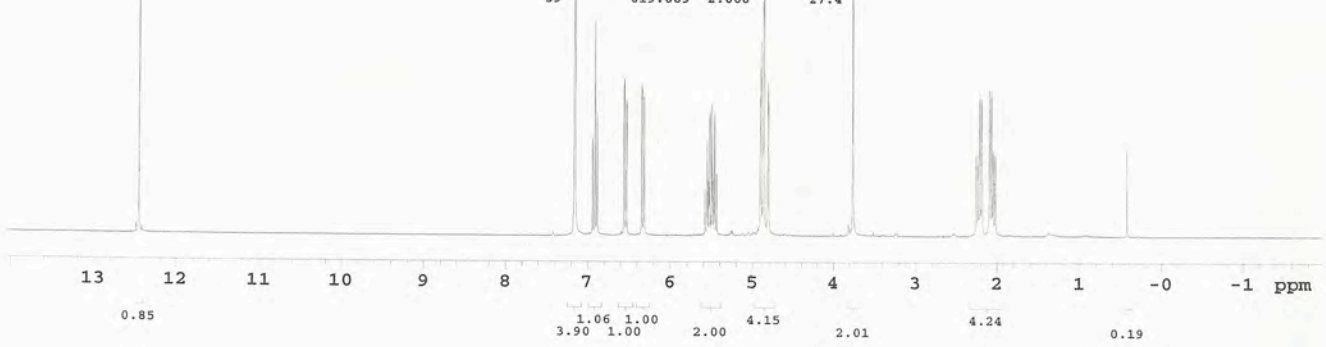
JGMM-XVI-2263 - Deallylation, chromanone

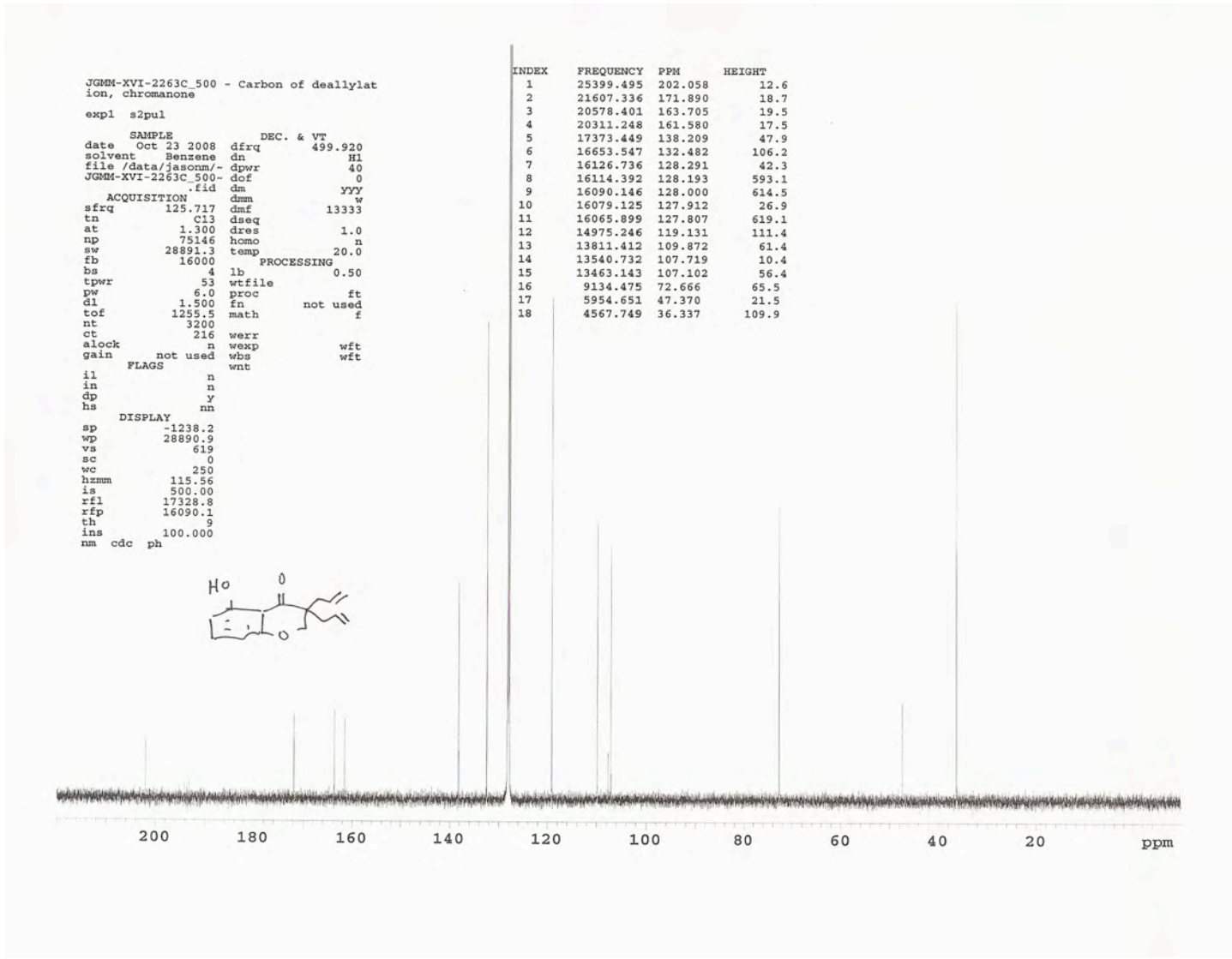
expl s2pul

SAMPLE		SPECIAL	
date	Oct 23 2008	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/-	spin	20
	JGMM-XVI-2263.fid	hst	0.008
ACQUISITION		pw90	14.000
sw	4789.3	alfa	-6.900
at	3.000	FLAGS	
np	28736	il	n
fb	not used	in	n
bs	2	dp	y
ss	2	hs	nn
d1	5.000	PROCESSING	
nt	320	lb	0.30
ct	16	fn	65536
TRANSMITTER		DISPLAY	
tn	H1	sp	-582.7
sfrq	299.763	wp	4789.1
tof	265.1	rf1	2729.1
tpwr	58	rfp	2146.3
pw	5.600	rp	123.3
DECOUPLER		lp	-6.9
dn	C13	PLOT	
dof	0	wc	250
dm	nnn	sc	0
dmm	c	vs	210
dpwr	46	th	9
dmf	13100	ai	ph



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3734.056	12.457	73.8	40	613.312	2.046	16.3
2	2146.353	7.160	126.0	41	605.858	2.021	15.5
3	2080.290	6.940	18.6	42	126.756	0.423	16.4
4	2071.959	6.912	40.9				
5	2063.774	6.885	23.3				
6	1965.703	6.558	29.2				
7	1964.826	6.555	29.8				
8	1957.372	6.530	25.8				
9	1956.495	6.527	25.2				
10	1901.540	6.344	28.8				
11	1900.663	6.341	28.0				
12	1893.355	6.316	26.5				
13	1892.478	6.313	25.1				
14	1665.204	5.555	17.8				
15	1662.427	5.546	10.6				
16	1657.750	5.530	10.3				
17	1655.119	5.521	23.8				
18	1648.250	5.499	24.9				
19	1645.619	5.490	12.9				
20	1640.942	5.474	11.5				
21	1638.165	5.465	23.3				
22	1630.711	5.440	11.8				
23	1470.085	4.904	26.6				
24	1469.061	4.901	31.8				
25	1468.038	4.897	36.9				
26	1460.000	4.871	44.6				
27	1458.830	4.867	63.8				
28	1457.954	4.864	57.4				
29	1443.338	4.815	14.3				
30	1441.876	4.810	29.0				
31	1439.976	4.804	25.5				
32	1438.661	4.799	12.8				
33	1127.931	3.763	153.5				
34	677.037	2.259	15.4				
35	669.729	2.234	15.5				
36	662.860	2.211	26.9				
37	655.552	2.187	26.2				
38	627.490	2.093	27.7				
39	619.889	2.068	27.4				



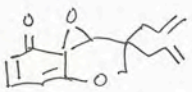

JGMM-XVI-2263C_500 - Carbon of deallylation, chromanone
expl s2pul
SAMPLE
date Oct 23 2008
solvent Benzene
file /data/jasonm/~
JGMM-XVI-2263C_500~
.fid
ACQUISITION
sfrq 125.717
tn C13
at 1.300
np 75146
sw 28891.3
fb 16000
bs 4
tpwr 53
pw 6.0
dl 1.500
tof 1255.5
nt 3200
ct 216
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1238.2
wp 28890.9
vs 619
sc 0
wc 250
hzmm 115.56
is 500.00
rfl 17328.8
rfp 16090.1
th 9
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.920
dn H1
dpwr 40
dof 0
dm yyy
dmm w
dmf 13333
dseq
dres 1.0
homo n
temp 20.0
PROCESSING
lb 0.50
wtfile
proc ft
fn not used
math f
werr
wexp wft
wbs wft
wnt
INDEX FREQUENCY PPM HEIGHT
1 25399.495 202.058 12.6
2 21607.336 171.890 18.7
3 20578.401 163.705 19.5
4 20311.248 161.580 17.5
5 17373.449 138.209 47.9
6 16653.547 132.482 106.2
7 16126.736 128.291 42.3
8 16114.392 128.193 593.1
9 16090.146 128.000 614.5
10 16079.125 127.912 26.9
11 16065.899 127.807 619.1
12 14975.246 119.131 111.4
13 13811.412 109.872 61.4
14 13540.732 107.719 10.4
15 13463.143 107.102 56.4
16 9134.475 72.666 65.5
17 5954.651 47.370 21.5
18 4567.749 36.337 109.9
HO
O
O
200
180
160
140
120
100
80
60
40
20
ppm

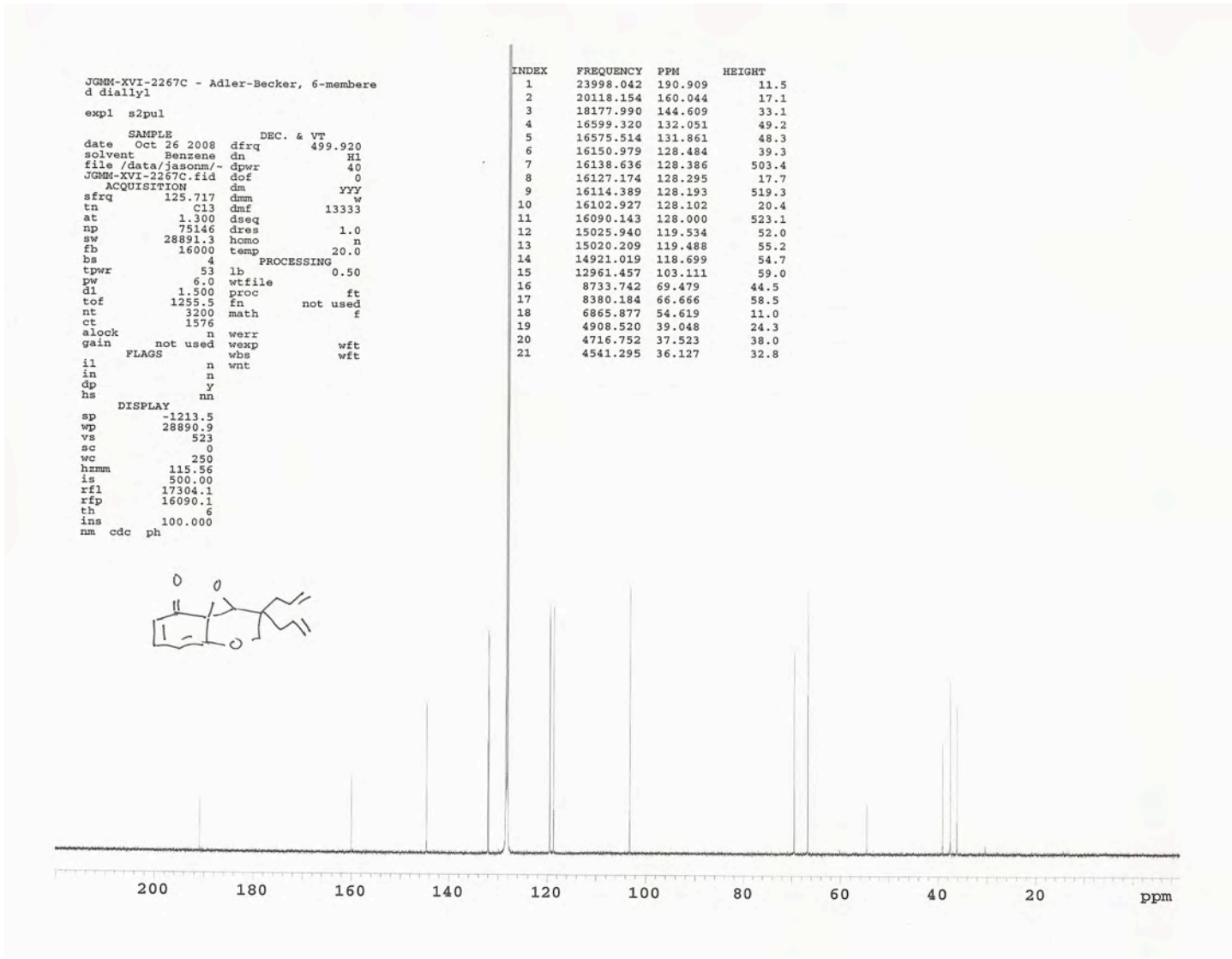
JGMM-XVI-2267 - Adler-Becker, 6-membered diallyl

expl s2pul

SAMPLE		DEC. & VT	
date	Oct 26 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/-	dpwr	30
	JGMM-XVI-2267.fid	dof	0
ACQUISITION		dm	nnn
sfrq	499.920	dmm	c
tn	H1	dmf	200
at	1.892	dseq	
np	30272	dres	1.0
sw	8000.0	homo	n
fb	4000	temp	20.0
bs	4	PROCESSING	
tpwr	58	wtfile	
pw	5.5	proc	ft
d1	6.000	fn	not used
tof	0	math	f
nt	320		
ct	8	werr	
alock	n	wexp	wft
gain	not used	wbs	wft
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	187		
sc	35		
wc	215		
hzmm	23.22		
is	33.57		
rfl	5073.2		
rfp	3579.4		
th	7		
ins	1.000		
nm	ph		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3579.408	7.160	187.3	40	2420.228	4.841	26.4
2	3249.330	6.500	35.0	41	2418.763	4.838	24.5
3	3242.005	6.485	34.3	42	2409.974	4.821	11.4
4	3239.564	6.480	37.4	43	2408.509	4.818	22.8
5	3232.240	6.466	36.1	44	2406.556	4.814	20.3
6	2898.744	5.798	44.6	45	2405.091	4.811	17.4
7	2888.978	5.779	41.9	46	2403.627	4.808	22.7
8	2753.724	5.508	44.5	47	2401.673	4.804	22.1
9	2750.794	5.502	9.4	48	2400.209	4.801	10.1
10	2746.888	5.495	43.2	49	1944.154	3.889	58.9
11	2743.470	5.488	14.5	50	1942.689	3.886	58.9
12	2741.029	5.483	9.5	51	1938.294	3.877	45.4
13	2736.146	5.473	7.8	52	1927.552	3.856	45.0
14	2733.705	5.468	17.5	53	1663.392	3.327	30.3
15	2726.380	5.454	17.0	54	1661.927	3.324	32.0
16	2723.939	5.449	9.3	55	1652.650	3.306	30.1
17	2719.056	5.439	8.7	56	1651.185	3.303	30.7
18	2716.615	5.434	15.2	57	880.189	1.761	7.0
19	2708.802	5.419	8.1	58	872.377	1.745	7.9
20	2705.873	5.413	7.2	59	866.029	1.732	59.8
21	2698.548	5.398	12.7	60	858.216	1.717	55.2
22	2696.107	5.393	7.6	61	856.263	1.713	53.0
23	2690.736	5.382	7.7	62	824.037	1.648	15.8
24	2688.294	5.377	16.3	63	459.779	0.920	7.4
25	2681.459	5.364	17.4	64	283.021	0.566	9.9
26	2679.017	5.359	9.6				
27	2674.134	5.349	8.5				
28	2671.205	5.343	14.5				
29	2663.880	5.329	8.9				
30	2452.943	4.907	22.1				
31	2450.990	4.903	24.1				
32	2442.201	4.885	42.0				
33	2441.224	4.883	44.5				
34	2431.947	4.865	21.4				
35	2430.970	4.863	21.5				
36	2429.994	4.861	24.6				
37	2425.599	4.852	26.5				
38	2423.646	4.848	23.8				
39	2422.181	4.845	18.4				



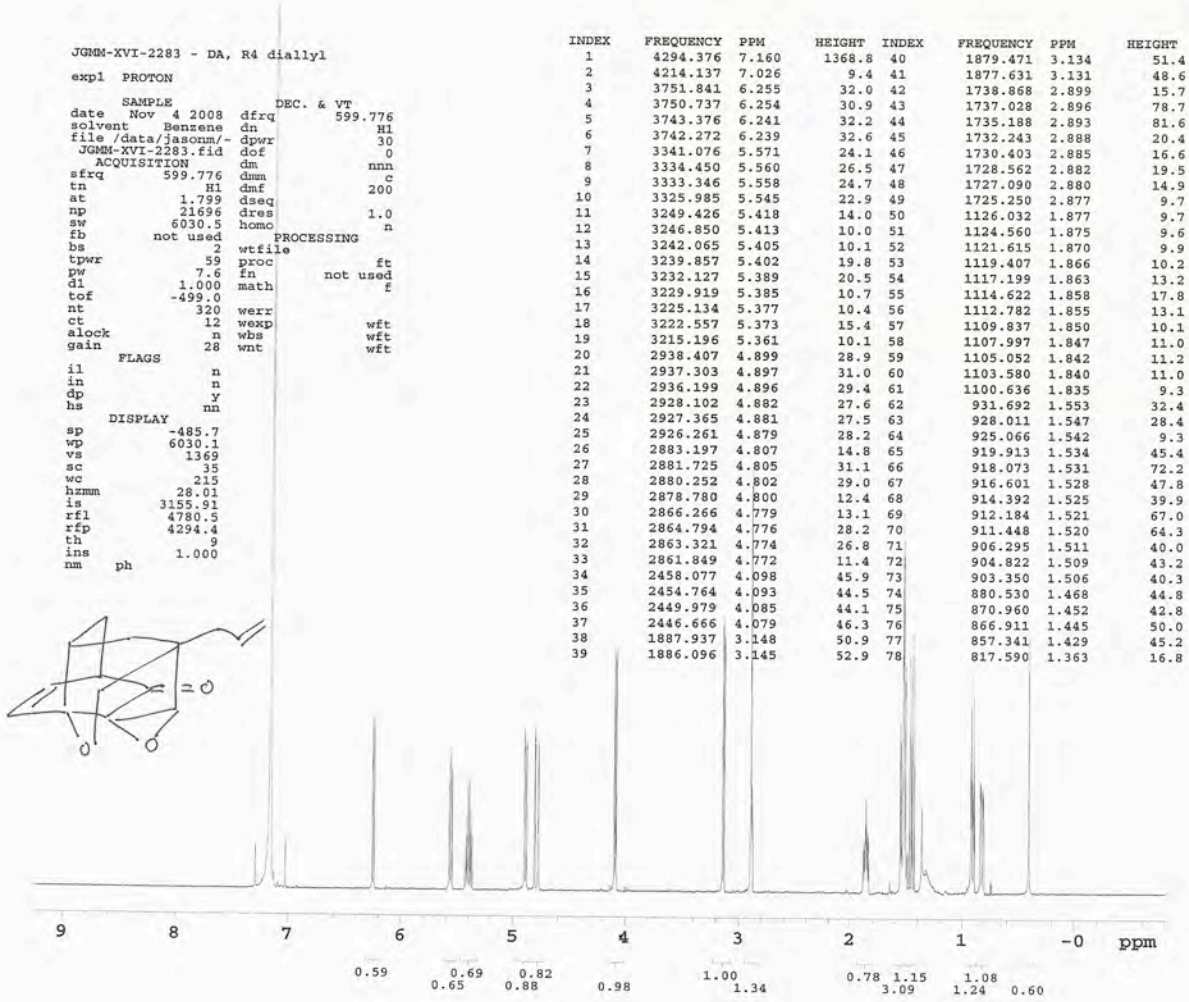

JGMM-XVI-2267C - Adler-Becker, 6-membere
d diallyl
expl s2pul
SAMPLE
date Oct 26 2008
solvent Benzene
file /data/jasonm/~
JGMM-XVI-2267C.fid
ACQUISITION
sfrq 125.717
tn C13
at 1.300
np 75146
sw 28891.3
fb 16000
bs 4
tpwr 53
pw 6.0
d1 1.500
tof 1255.5
nt 3200
ct 1576
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1213.5
wp 28890.9
vs 523
sc 0
wc 250
hzmm 115.56
is 500.00
rfl 17304.1
rfp 16090.1
th 6
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.920
dn H1
dpwr 40
dof 0
dm yyy
dmm w
dmf 13333
dseq
dres 1.0
homo n
temp 20.0
PROCESSING
lb 0.50
wtfile
proc ft
fn not used
math f
werr
wexp wft
wbs wft
wnt
INDEX FREQUENCY PPM HEIGHT
1 23998.042 190.909 11.5
2 20118.154 160.044 17.1
3 18177.990 144.609 33.1
4 16599.320 132.051 49.2
5 16575.514 131.861 48.3
6 16150.979 128.484 39.3
7 16138.636 128.386 503.4
8 16127.174 128.295 17.7
9 16114.389 128.193 519.3
10 16102.927 128.102 20.4
11 16090.143 128.000 523.1
12 15025.940 119.534 52.0
13 15020.209 119.488 55.2
14 14921.019 118.699 54.7
15 12961.457 103.111 59.0
16 8733.742 69.479 44.5
17 8380.184 66.666 58.5
18 6865.877 54.619 11.0
19 4908.520 39.048 24.3
20 4716.752 37.523 38.0
21 4541.295 36.127 32.8
O
O
200
180
160
140
120
100
80
60
40
20
ppm

JGMM-XVI-2283 - DA, R4 diallyl

expl PROTON

SAMPLE		DEC. & VT	
date	Nov 4 2008	dfrq	599.776
solvent	Benzene	dn	H1
file	/data/jasonm/-	dpwr	30
	JGMM-XVI-2283.fid	dof	0
ACQUISITION		dm	nnn
sfrq	599.776	dmm	c
tn	H1	dmf	200
at	1.799	dseq	
np	21696	dres	1.0
sw	6030.5	homo	n
fb	not used	PROCESSING	
bs	2	wtfile	
tpwr	59	proc	ft
pw	7.6	fn	not used
d1	1.000	math	f
tof	-499.0		
nt	320	werr	
ct	12	wexp	wft
alock	n	wbs	wft
gain	28	wnt	wft
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-485.7		
wp	6030.1		
vs	1369		
sc	35		
wc	215		
hzmm	28.01		
is	3155.91		
rfl	4780.5		
rfp	4294.4		
th	9		
ins	1.000		
nm	ph		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM
1	4294.376	7.160	1368.8	40	1879.471	3.134	51.4	79	553.316	0.923
2	4214.137	7.026	9.4	41	1877.631	3.131	48.6	80	550.371	0.918
3	3751.841	6.255	32.0	42	1738.868	2.899	15.7	81	547.427	0.913
4	3750.737	6.254	30.9	43	1737.028	2.896	78.7	82	539.697	0.900
5	3743.376	6.241	32.2	44	1735.188	2.893	81.6	83	536.753	0.895
6	3742.272	6.239	32.6	45	1732.243	2.888	20.4	84	533.440	0.889
7	3341.076	5.571	24.1	46	1730.403	2.885	16.6	85	503.626	0.840
8	3334.450	5.560	26.5	47	1728.562	2.882	19.5	86	501.786	0.837
9	3333.346	5.558	24.7	48	1727.090	2.880	14.9	87	499.210	0.832
10	3325.985	5.545	22.9	49	1725.250	2.877	9.7	88	497.369	0.829
11	3249.426	5.418	14.0	50	1126.032	1.877	9.7	89	490.008	0.817
12	3246.850	5.413	10.0	51	1124.560	1.875	9.6	90	488.168	0.814
13	3242.065	5.405	10.1	52	1121.615	1.870	9.9	91	485.591	0.810
14	3239.857	5.402	19.8	53	1119.407	1.866	10.2	92	483.751	0.807
15	3232.127	5.389	20.5	54	1117.199	1.863	13.2	93	240.825	0.402
16	3229.919	5.385	10.7	55	1114.622	1.858	17.8			
17	3225.134	5.377	10.4	56	1112.782	1.855	13.1			
18	3222.557	5.373	15.4	57	1109.837	1.850	10.1			
19	3215.196	5.361	10.1	58	1107.997	1.847	11.0			
20	2938.407	4.899	28.9	59	1105.052	1.842	11.2			
21	2937.303	4.897	31.0	60	1103.580	1.840	11.0			
22	2936.199	4.896	29.4	61	1100.636	1.835	9.3			
23	2928.102	4.882	27.6	62	931.692	1.553	32.4			
24	2927.365	4.881	27.5	63	928.011	1.547	28.4			
25	2926.261	4.879	28.2	64	925.066	1.542	9.3			
26	2883.197	4.807	14.8	65	919.913	1.534	45.4			
27	2881.725	4.805	31.1	66	918.073	1.531	72.2			
28	2880.252	4.802	29.0	67	916.601	1.528	47.8			
29	2878.780	4.800	12.4	68	914.392	1.525	39.9			
30	2866.266	4.779	13.1	69	912.184	1.521	67.0			
31	2864.794	4.776	28.2	70	911.448	1.520	64.3			
32	2863.321	4.774	26.8	71	906.295	1.511	40.0			
33	2861.849	4.772	11.4	72	904.822	1.509	43.2			
34	2458.077	4.098	45.9	73	903.350	1.506	40.3			
35	2454.764	4.093	44.5	74	880.530	1.468	44.8			
36	2449.979	4.085	44.1	75	870.960	1.452	42.8			
37	2446.666	4.079	46.3	76	866.911	1.445	50.0			
38	1887.937	3.148	50.9	77	857.341	1.429	45.2			
39	1886.096	3.145	52.9	78	817.590	1.363	16.8			

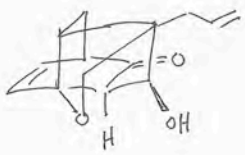


JGMM-XVI-2312 - 2nd attempt at Cp2TiCl opening of R4 diallyl bicycle epoxide, after column

expl PROTON

SAMPLE		DEC. & VT	
date	Nov 25 2008	dfrq	599.776
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
	JGMM-XVI-2312.fid	dof	0
ACQUISITION		dm	nnn
sfrq	599.776	dmm	c
tn	H1	dmf	200
at	1.892	dseq	
np	30272	dres	1.0
sw	8000.0	homo	n
fb	not used	PROCESSING	
bs	2	wtfile	
tpwr	59	proc	ft
pw	5.5	fn	not used
dl	0	math	f
tof	0		
nt	320	werr	
ct	48	wexp	wft
alock	n	wbs	wft
gain	not used	wnt	wft
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-300.4		
wp	5997.6		
vs	3660		
sc	35		
wc	215		
hzmm	27.86		
is	33.57		
rfl	5265.6		
rfp	4294.4		
th	7		
ins	2.000		
nm	ph		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM
1	4372.501	7.290	24.2	40	2476.993	4.130	30.8	79	886.661	1.478
2	4294.376	7.160	3659.8	41	2471.622	4.121	27.2	80	817.814	1.364
3	4273.380	7.125	7.9	42	2468.204	4.115	30.4	81	792.911	1.322
4	4274.357	7.127	8.1	43	2160.587	3.602	18.1	82	552.677	0.923
5	4214.298	7.026	24.9	44	2031.193	3.387	35.8	83	482.853	0.805
6	3802.189	6.339	16.2	45	2029.239	3.383	33.2	84	479.923	0.800
7	3801.212	6.338	17.3	46	2022.404	3.372	35.3	85	476.993	0.795
8	3793.888	6.326	17.8	47	2020.939	3.370	29.0	86	473.087	0.789
9	3792.423	6.323	16.6	48	1697.697	2.831	10.8	87	470.157	0.784
10	3580.021	5.969	73.2	49	1693.302	2.823	10.7	88	467.228	0.779
11	3363.224	5.607	14.1	50	1691.349	2.820	11.1	89	459.415	0.766
12	3357.364	5.598	14.4	51	1690.372	2.818	10.5	90	455.997	0.760
13	3354.923	5.594	13.6	52	1328.556	2.215	17.2	91	454.532	0.758
14	3349.064	5.584	13.8	53	1325.626	2.210	32.8	92	451.603	0.753
15	3296.818	5.497	10.4	54	1322.697	2.205	16.6	93	244.083	0.407
16	3289.005	5.484	7.4	55	1123.966	1.874	13.1			
17	3286.564	5.480	15.3	56	1116.154	1.861	13.7			
18	3279.728	5.468	15.7	57	1110.294	1.851	15.7			
19	3277.286	5.464	7.2	58	1102.482	1.838	15.1			
20	3269.474	5.451	14.8	59	1058.536	1.765	7.8			
21	3262.150	5.439	7.1	60	1055.607	1.760	10.3			
22	2962.345	4.939	9.6	61	1054.142	1.758	7.5			
23	2961.368	4.937	19.0	62	1052.189	1.754	7.5			
24	2960.392	4.936	14.6	63	1050.724	1.752	10.2			
25	2958.927	4.933	19.1	64	1047.794	1.747	9.1			
26	2951.114	4.920	16.1	65	964.298	1.608	31.8			
27	2950.138	4.919	14.7	66	953.068	1.589	27.9			
28	2949.161	4.917	17.7	67	950.138	1.584	33.7			
29	2928.654	4.883	10.1	68	939.396	1.566	28.1			
30	2927.189	4.880	22.0	69	936.954	1.562	17.8			
31	2926.212	4.879	14.7	70	929.142	1.549	18.1			
32	2924.747	4.876	17.2	71	923.282	1.539	15.3			
33	2923.771	4.875	7.4	72	914.493	1.525	23.5			
34	2911.564	4.854	9.4	73	911.075	1.519	17.9			
35	2910.099	4.852	17.2	74	902.775	1.505	25.4			
36	2909.122	4.850	14.2	75	900.822	1.502	25.5			
37	2908.146	4.849	15.3	76	899.845	1.500	28.2			
38	2906.681	4.846	8.2	77	897.892	1.497	24.3			
39	2479.923	4.135	28.8	78	889.591	1.483	15.4			

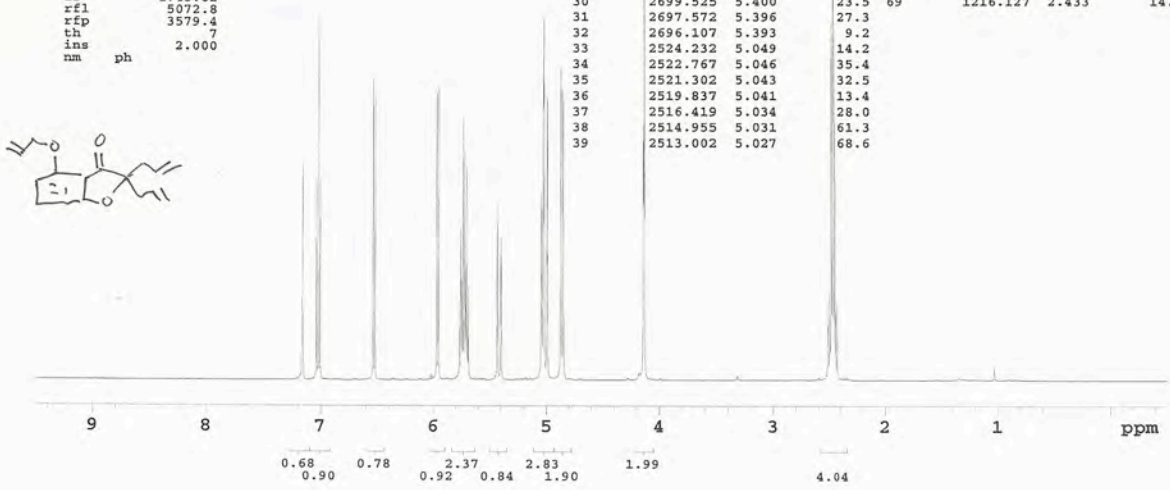


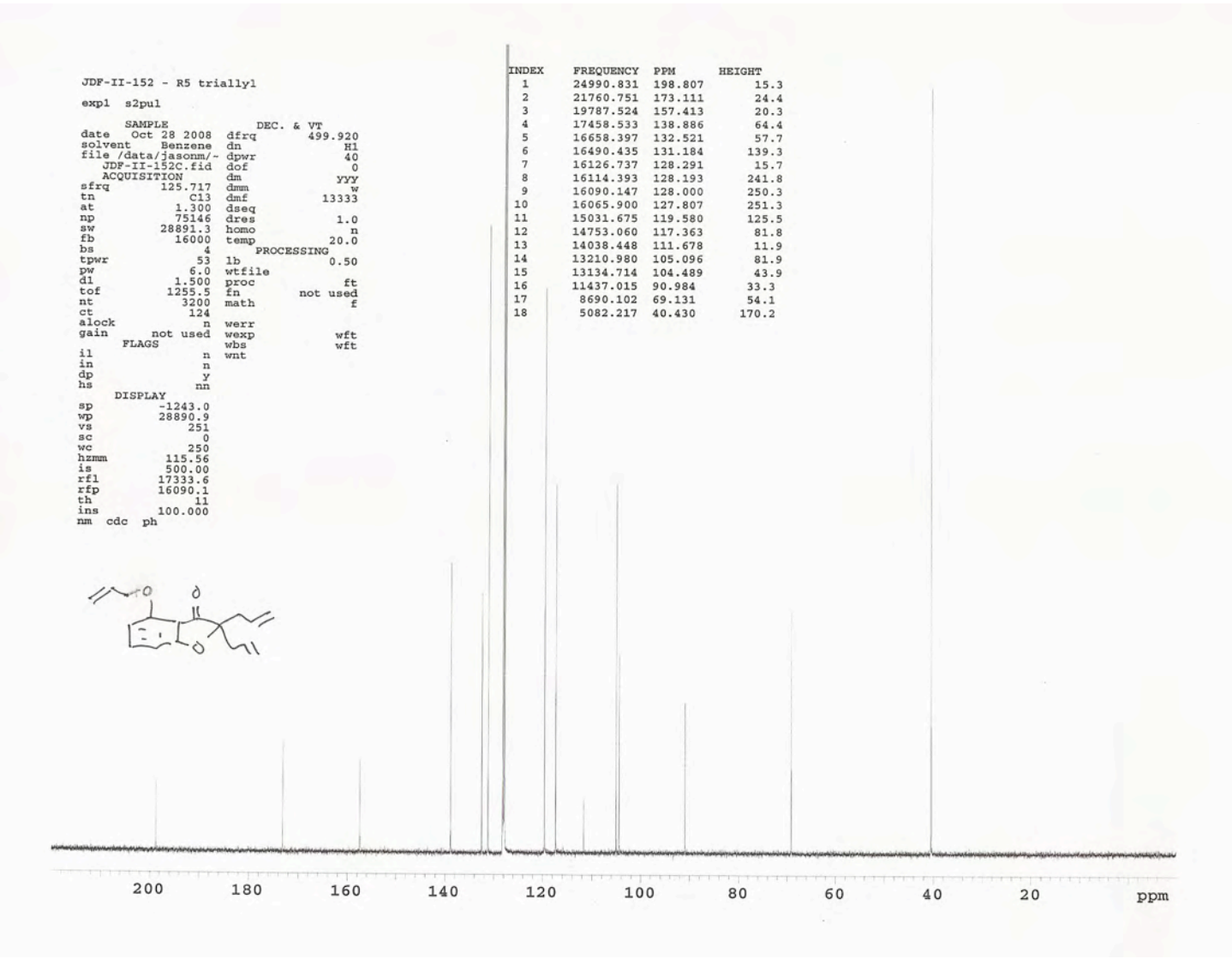
JDF-II-152 - R5 triallyl

expl s2pul

SAMPLE		DEC. & VT	
date	Oct 28 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/-	dpwr	30
	JDF-II-152.fid	dof	0
ACQUISITION		dm	nnn
sfrq	499.920	dmm	c
tn	H1	dmf	200
at	1.892	dseq	
np	30272	dres	1.0
sw	8000.0	homo	n
fb	4000	temp	20.0
bs	2	PROCESSING	
tpwr	58	wtfile	
pw	5.5	proc	ft
d1	2.000	fn	not used
tof	0	math	f
nt	320		
ct	8	werr	
alock	n	wexp	wft
gain	not used	wbs	wft
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	121		
sc	35		
wc	215		
hzmm	23.22		
is	1745.82		
rfl	5072.8		
rfp	3579.4		
th	7		
ins	2.000		
nm	ph		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3579.408	7.160	41.0	40	2512.025	5.025	56.7
2	3518.373	7.038	38.2	41	2510.560	5.022	39.1
3	3510.072	7.021	69.6	42	2509.095	5.019	14.4
4	3502.259	7.006	37.9	43	2499.330	4.999	24.4
5	3268.861	6.539	57.1	44	2497.865	4.997	53.8
6	3260.560	6.522	53.8	45	2495.912	4.993	53.1
7	2984.681	5.970	54.8	46	2494.447	4.990	23.8
8	2976.380	5.954	55.4	47	2437.806	4.876	59.3
9	2884.584	5.770	14.6	48	2436.830	4.874	54.7
10	2883.607	5.768	9.6	49	2435.853	4.873	55.5
11	2878.724	5.758	19.1	50	2427.552	4.856	55.3
12	2877.748	5.756	29.2	51	2426.576	4.854	51.5
13	2874.818	5.751	19.2	52	2425.599	4.852	52.7
14	2870.423	5.742	17.7	53	2072.084	4.145	45.4
15	2867.494	5.736	49.9	54	2070.619	4.142	79.5
16	2863.587	5.728	11.3	55	2068.666	4.138	48.8
17	2861.634	5.724	28.0	56	2067.201	4.135	48.3
18	2860.658	5.722	43.8	57	2065.736	4.132	80.3
19	2857.728	5.716	21.2	58	2063.783	4.128	40.0
20	2855.775	5.712	14.1	59	1259.584	2.520	10.3
21	2853.334	5.708	19.5	60	1258.607	2.518	14.7
22	2850.404	5.702	40.1	61	1257.142	2.515	9.1
23	2846.009	5.693	10.0	62	1251.283	2.503	16.5
24	2843.080	5.687	17.5	63	1244.447	2.489	67.9
25	2718.080	5.437	11.8	64	1237.123	2.475	120.9
26	2716.615	5.434	33.3	65	1230.287	2.461	68.0
27	2714.662	5.430	29.8	66	1224.427	2.449	11.6
28	2713.197	5.427	12.8	67	1223.451	2.447	16.0
29	2700.990	5.403	10.5	68	1217.103	2.435	10.0
30	2699.525	5.400	23.5	69	1216.127	2.433	14.2
31	2697.572	5.396	27.3				
32	2696.107	5.393	9.2				
33	2524.232	5.049	14.2				
34	2522.767	5.046	35.4				
35	2521.302	5.043	32.5				
36	2519.837	5.041	13.4				
37	2516.419	5.034	28.0				
38	2514.955	5.031	61.3				
39	2513.002	5.027	68.6				

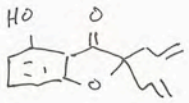



JDF-II-152 - R5 triallyl
expl s2pul
SAMPLE
date Oct 28 2008
solvent Benzene
file /data/jasonm/~
JDF-II-152C.fid
ACQUISITION
sfrq 125.717
tn C13
at 1.300
np 75146
sw 28891.3
fb 16000
bs 4
tpwr 53
pw 6.0
d1 1.500
tof 1255.5
nt 3200
ct 124
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1243.0
wp 28890.9
vs 251
sc 0
wc 250
hzmm 115.56
is 500.00
rfl 17333.6
rfp 16090.1
th 11
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.920
dn H1
dpwr 40
dof 0
dm yyy
dmm w
dmf 13333
dseq
dres 1.0
homo n
temp 20.0
PROCESSING
lb 0.50
wtfile
proc ft
fn not used
math f
werr
wexp wft
wbs wft
wnt
INDEX FREQUENCY PPM HEIGHT
1 24990.831 198.807 15.3
2 21760.751 173.111 24.4
3 19787.524 157.413 20.3
4 17458.533 138.886 64.4
5 16658.397 132.521 57.7
6 16490.435 131.184 139.3
7 16126.737 128.291 15.7
8 16114.393 128.193 241.8
9 16090.147 128.000 250.3
10 16065.900 127.807 251.3
11 15031.675 119.580 125.5
12 14753.060 117.363 81.8
13 14038.448 111.678 11.9
14 13210.980 105.096 81.9
15 13134.714 104.489 43.9
16 11437.015 90.984 33.3
17 8690.102 69.131 54.1
18 5082.217 40.430 170.2
200
180
160
140
120
100
80
60
40
20
ppm

JGMM-XVI-2279_500 - R5 diallyl

expl s2pul

SAMPLE		DEC. & VT	
date	Oct 30 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/-	dpwr	30
JGMM-XVI-2279_500.-		dof	0
	fid	dm	nnn
ACQUISITION		dmm	c
sfrq	499.920	dmf	200
tn	H1	dseq	
at	1.500	dres	1.0
np	24000	homo	n
sw	8000.0	temp	20.0
fb	4000	PROCESSING	
bs	2	wtfile	
tpwr	58	proc	ft
pw	5.5	fn	not used
d1	5.000	math	f
tof	0		
nt	8	werr	
ct	8	wexp	wft
alock	n	wbs	wft
gain	not used	wnt	wft
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	122		
sc	35		
wc	215		
hzmm	23.22		
is	33.57		
rfl	5072.8		
rfp	3579.4		
th	9		
ins	1.000		
nm	ph		



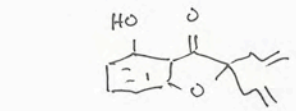
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	4064.271	8.130	19.2	40	1188.294	2.377	105.4
2	3579.408	7.160	70.2	41	1184.877	2.370	74.0
3	3465.150	6.931	57.3	42	1183.900	2.368	104.2
4	3456.849	6.915	121.8	43	1182.435	2.365	97.1
5	3448.548	6.898	58.4	44	1180.970	2.362	103.4
6	3165.345	6.332	86.1	45	1173.646	2.348	11.0
7	3157.044	6.315	82.7	46	1166.322	2.333	9.6
8	3151.185	6.303	92.8				
9	3142.884	6.287	89.8				
10	2831.849	5.665	22.4				
11	2824.525	5.650	45.5				
12	2821.595	5.644	23.9				
13	2817.201	5.635	23.1				
14	2814.759	5.630	62.5				
15	2807.435	5.616	69.8				
16	2804.505	5.610	25.3				
17	2800.111	5.601	23.2				
18	2797.669	5.596	46.2				
19	2790.345	5.582	25.4				
20	2500.306	5.001	35.7				
21	2498.841	4.999	77.2				
22	2497.377	4.996	81.2				
23	2495.912	4.993	39.0				
24	2483.216	4.967	31.4				
25	2481.752	4.964	68.5				
26	2480.287	4.961	75.6				
27	2478.822	4.958	36.2				
28	2434.877	4.871	82.4				
29	2433.900	4.869	80.7				
30	2432.923	4.867	80.6				
31	2424.623	4.850	79.1				
32	2423.646	4.848	76.6				
33	2422.669	4.846	76.0				
34	1205.384	2.411	11.9				
35	1203.919	2.408	9.4				
36	1199.037	2.398	11.9				
37	1198.060	2.397	15.3				
38	1190.736	2.382	107.4				
39	1189.271	2.379	101.7				

JGMM-XVI-2279C_500 - Carbon, R5 diallyl

expl s2pul

SAMPLE		DEC. & VT	
date	Oct 30 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/-	dpwr	40
	JGMM-XVI-2279C_500~	dof	0
	.fid	dm	yyy
ACQUISITION		dmm	w
sfrq	125.717	dmf	13333
tn	C13	dseq	
at	0.500	dres	1.0
np	28892	homo	n
sw	28891.3	temp	20.0
fb	16000	PROCESSING	
bs	8	lb	0.50
tpwr	53	wtfile	
pw	6.0	proc	ft
d1	3.000	fn	not used
tof	1255.5	math	f
nt	3200		
ct	112	werr	
alock	n	wexp	wft
gain	not used	wbs	wft
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1236.9		
wp	28889.5		
vs	275		
sc	0		
wc	250		
hzmm	115.56		
is	500.00		
rfl	17328.8		
rfp	16090.1		
th	5		
ins	100.000		
nm cdc ph			

INDEX	FREQUENCY	PPM	HEIGHT
1	25647.691	204.032	13.9
2	21491.394	170.968	7.0
3	19728.009	156.940	9.8
4	17677.192	140.625	41.3
5	16419.899	130.623	100.8
6	16127.177	128.295	13.6
7	16114.833	128.196	226.8
8	16090.146	128.000	263.3
9	16077.802	127.902	10.4
10	16065.458	127.804	274.7
11	15070.909	119.892	136.9
12	13806.563	109.834	5.3
13	13552.635	107.814	58.8
14	13028.910	103.647	54.3
15	11537.086	91.780	21.5
16	5001.982	39.792	103.0

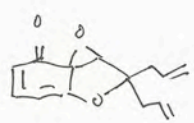


JGMM-XVI-2274a1 - Repurification of Adle
r-Becker, diallyl R5

expl s2pul

SAMPLE		SPECIAL	
date	Oct 29 2008	temp	not used
solvent	Benzene	gain	not used
file	/data/jascnm/-	spin	not used
JGMM-XVI-2274a1.fi-		hst	0.008
	d	pw90	8.400
ACQUISITION		alfa	1.600
sw	6387.7	FLAGS	
at	2.565	il	n
np	32768	in	n
fb	not used	dp	y
bs	2	hs	nn
d1	2.000	PROCESSING	
nt	320	lb	0.30
ct	16	fn	not used
TRANSMITTER		DISPLAY	
tn	H1	sp	-200.1
sfrq	399.780	wp	3997.4
tof	399.5	rf1	3627.8
tpwr	59	rfp	2862.4
pw	4.200	rp	170.2
DECOUPLER		lp	8.0
dn	C13	is	500
dof	0	PLOT	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	33	vs	298
dmf	29412	th	11
		ai ph	

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2862.406	7.160	1360.9	40	795.281	1.989	25.7
2	2558.302	6.399	34.4	41	787.873	1.971	25.6
3	2551.674	6.383	35.7	42	744.207	1.862	24.9
4	2548.166	6.374	34.5	43	737.189	1.844	25.4
5	2541.538	6.357	35.1	44	729.782	1.825	17.6
6	2293.186	5.736	59.2	45	722.374	1.807	16.6
7	2283.050	5.711	53.4	46	544.591	1.362	12.2
8	2238.214	5.599	12.2	47	164.461	0.411	31.9
9	2228.467	5.574	15.6				
10	2221.059	5.556	14.6				
11	2218.720	5.550	11.9				
12	2210.922	5.530	14.7				
13	2168.816	5.425	14.6				
14	2158.679	5.400	22.3				
15	2151.661	5.382	23.8				
16	2141.524	5.357	17.9				
17	2068.617	5.174	56.9				
18	2061.990	5.158	56.7				
19	1987.133	4.971	37.3				
20	1983.624	4.962	38.6				
21	1971.538	4.932	61.8				
22	1945.027	4.865	33.8				
23	1935.670	4.842	29.3				
24	1934.890	4.840	29.8				
25	1917.735	4.797	30.6				
26	1916.176	4.793	31.1				
27	1900.581	4.754	27.1				
28	1899.021	4.750	26.8				
29	1667.045	4.170	128.1				
30	977.743	2.446	11.3				
31	970.725	2.428	11.6				
32	964.098	2.412	29.7				
33	957.080	2.394	29.6				
34	948.892	2.374	30.7				
35	941.095	2.354	30.5				
36	935.247	2.339	11.9				
37	927.449	2.320	11.5				
38	809.706	2.025	16.6				
39	802.299	2.007	16.5				

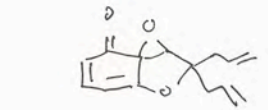


JGMM-XVI-2274a1 - Adler-Becker, R5 diallyl

expl s2pul

SAMPLE		DEC. & VT	
date	Oct 30 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	40
JGMM-XVI-2274a1C2.~		dof	0
	fid	dm	yyy
ACQUISITION		dmm	w
sfrq	125.717	dmf	13333
tn	C13	dseq	
at	1.300	dres	1.0
np	75146	homo	n
sw	28891.3	temp	20.0
fb	16000	PROCESSING	
bs	4	lb	0.52
tpwr	53	wtfile	
pw	6.0	proc	ft
dl	1.500	fn	not used
tof	1255.5	math	f
nt	9999		
ct	2768	werr	
alock	n	wexp	wft
gain	not used	wbs	wft
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	850.1		
wp	24334.7		
vs	2766		
sc	0		
wc	250		
hzmm	97.34		
is	500.00		
rfl	17328.3		
rfp	16090.1		
th	7		
ins	100.000		
nm	ph		

INDEX	FREQUENCY	PPM	HEIGHT
1	23894.005	190.081	7.9
2	20695.225	164.634	12.3
3	18253.378	145.209	31.4
4	16579.926	131.896	42.0
5	16388.358	130.371	38.4
6	16127.177	128.295	231.8
7	16114.392	128.193	2651.3
8	16103.371	128.105	111.2
9	16090.146	128.000	2746.8
10	16079.125	127.912	126.1
11	16065.899	127.807	2766.4
12	16025.782	127.488	7.6
13	15109.263	120.197	47.6
14	15041.373	119.657	40.5
15	15014.922	119.446	54.6
16	12260.074	97.531	44.1
17	11324.158	90.086	20.1
18	8461.302	67.311	48.9
19	7624.135	60.651	8.7
20	4954.812	39.416	55.8
21	4774.946	37.986	54.6

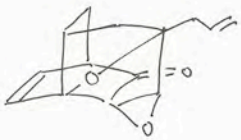


JGMM-XVI-2280a - DA, R5 diallyl

expl PROTON

SAMPLE		DEC. & VT	
date	Oct 31 2008	dfrq	599.776
solvent	Benzene	dn	H1
file	/data/jasonm/-	dpwr	30
	JGMM-XVI-2280b.fid	dof	0
ACQUISITION		dm	nnn
sfrq	599.776	dmm	c
tn	H1	dmf	200
at	1.892	dseq	
np	30272	dres	1.0
sw	8000.0	homo	n
fb	not used	temp	25.0
bs	4	PROCESSING	
tpwr	59	wtfile	
pw	5.5	proc	ft
d1	5.000	fn	not used
tof	0	math	f
nt	320		
ct	12	werr	
alock	n	wexp	wft
gain	not used	wbs	wft
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-300.4		
wp	5997.6		
vs	2019		
sc	35		
wc	215		
hzmm	27.86		
is	33.57		
rfl	5266.1		
rfp	4294.4		
th	11		
ins	2.000		
nm	ph		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	4372.013	7.289	11.9	40	832.462	1.388	33.2
2	4294.376	7.160	2018.9	41	822.208	1.371	31.1
3	4213.810	7.026	13.1	42	817.325	1.363	21.2
4	3847.599	6.415	37.0	43	802.677	1.338	19.4
5	3838.810	6.400	41.9	44	798.282	1.331	17.6
6	3466.739	5.780	13.0	45	790.958	1.319	19.8
7	3456.486	5.763	16.8	46	789.005	1.316	23.4
8	3449.650	5.752	16.2	47	787.052	1.312	18.3
9	3439.396	5.734	13.7	48	784.611	1.308	20.4
10	3276.798	5.463	24.1	49	777.286	1.296	19.1
11	3270.450	5.453	27.5	50	773.380	1.289	17.6
12	3268.497	5.450	24.6	51	662.052	1.104	19.0
13	3261.661	5.438	22.1	52	655.704	1.093	17.9
14	2999.943	5.002	31.7	53	648.380	1.081	15.1
15	2998.966	5.000	39.4	54	642.032	1.070	14.3
16	2997.989	4.999	32.2	55	362.736	0.605	28.3
17	2996.525	4.996	33.8	56	357.853	0.597	27.6
18	2995.060	4.994	21.7	57	350.040	0.584	27.1
19	2990.665	4.986	23.3	58	345.646	0.576	25.6
20	2989.689	4.985	26.1	59	238.224	0.397	38.3
21	2988.712	4.983	24.6				
22	2979.435	4.968	26.0				
23	2977.970	4.965	20.6				
24	1822.697	3.039	115.9				
25	1788.517	2.982	16.9				
26	1784.611	2.975	19.1				
27	1783.146	2.973	20.6				
28	1782.169	2.971	16.9				
29	1779.239	2.967	13.6				
30	1778.263	2.965	15.5				
31	1437.443	2.397	26.2				
32	1430.118	2.384	26.4				
33	1420.353	2.368	25.7				
34	1413.517	2.357	25.0				
35	990.665	1.652	15.8				
36	984.806	1.642	17.5				
37	978.947	1.632	16.0				
38	844.669	1.408	30.0				
39	834.415	1.391	29.9				

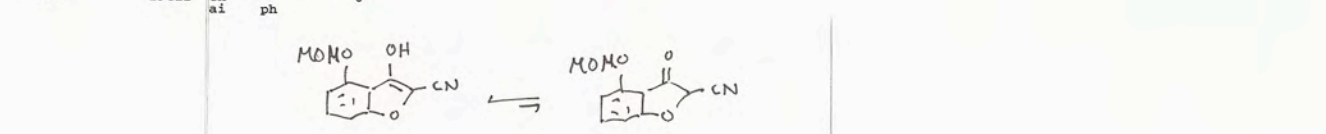


JGMM-X-1468x - Crude of att. Dieckmann

exp1 s2pul

SAMPLE		SPECIAL	
date	Jan 19 2007	temp	not used
solvent	Benzene	gain	not used
file	/data/jasonm/--	spin	20
	JasonMBook10/JGMM--	hst	0.008
	X-1468x.fid	pw90	8.400
ACQUISITION		alfa	1.600
sw	6387.7	FLAGS	
at	3.000	il	n
np	38326	in	n
fb	not used	dp	y
bs	2	hs	nn
d1	1.000	PROCESSING	
nt	32	lb	0.30
ct	18	fn	not used
TRANSMITTER		DISPLAY	
tn	H1	sp	-200.1
sfrq	399.780	wp	3598.0
tof	399.5	rfl	3627.6
tpwr	58	rfp	2862.4
pw	4.200	rp	-51.5
DECOUPLER		lp	8.8
dn	C13	is	500
dof	0	PLOT	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	33	vs	66
dmf	29412	th	6
		ai	ph

INDEX	FREQUENCY	PPM	HEIGHT
1	2862.406	7.160	369.8
2	2719.126	6.802	11.1
3	2710.744	6.781	24.5
4	2705.286	6.767	8.8
5	2702.557	6.760	15.7
6	2640.176	6.604	26.7
7	2631.599	6.583	21.5
8	2604.113	6.514	24.0
9	2595.925	6.493	20.8
10	2533.155	6.336	7.8
11	2524.968	6.316	7.1
12	2460.248	6.154	7.5
13	2452.061	6.134	7.0
14	1880.112	4.703	29.5
15	1775.430	4.441	40.5
16	1574.449	3.938	14.7
17	1206.796	3.019	46.7
18	1147.534	2.870	83.3



JGMM-XI-1528 - Alkylation of R5 cyano

expl s2pul

SAMPLE		DEC. & VT	
date	Nov 2 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
JGMM-Char2-XI-1528~	.fid	dof	0
ACQUISITION		dm	nnn
		dmm	c
sfrq	499.920	dmf	200
tn	H1	dseq	
at	1.000	dres	1.0
np	16000	homo	n
sw	8000.0	temp	20.0
fb	4000	PROCESSING	
bs	4	wtfile	
tpwr	58	proc	ft
pw	5.5	fn	not used
d1	5.000	math	f
tof	0		
nt	320	werr	
ct	4	wexp	wft
alock	n	wbs	wft
gain	not used	wnt	wft
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-30.9		
wp	4345.7		
vs	151		
sc	35		
wc	215		
hzmm	20.19		
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7	3187.806	6.377	23.0
8	3179.994	6.361	23.1
9	3109.681	6.220	20.1
10	3100.892	6.203	25.0
11	2358.705	4.718	65.1
12	1941.712	3.884	8.8
13	1933.900	3.868	29.1
14	1927.064	3.855	30.4
15	1920.228	3.841	10.6
16	1509.095	3.019	151.2
17	1364.564	2.730	6.4
18	1348.939	2.698	7.7
19	1342.103	2.685	6.8
20	1202.455	2.405	7.8
21	1194.642	2.390	7.5
22	1186.830	2.374	6.6
23	1179.017	2.358	6.2
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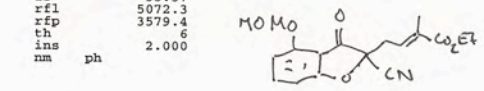

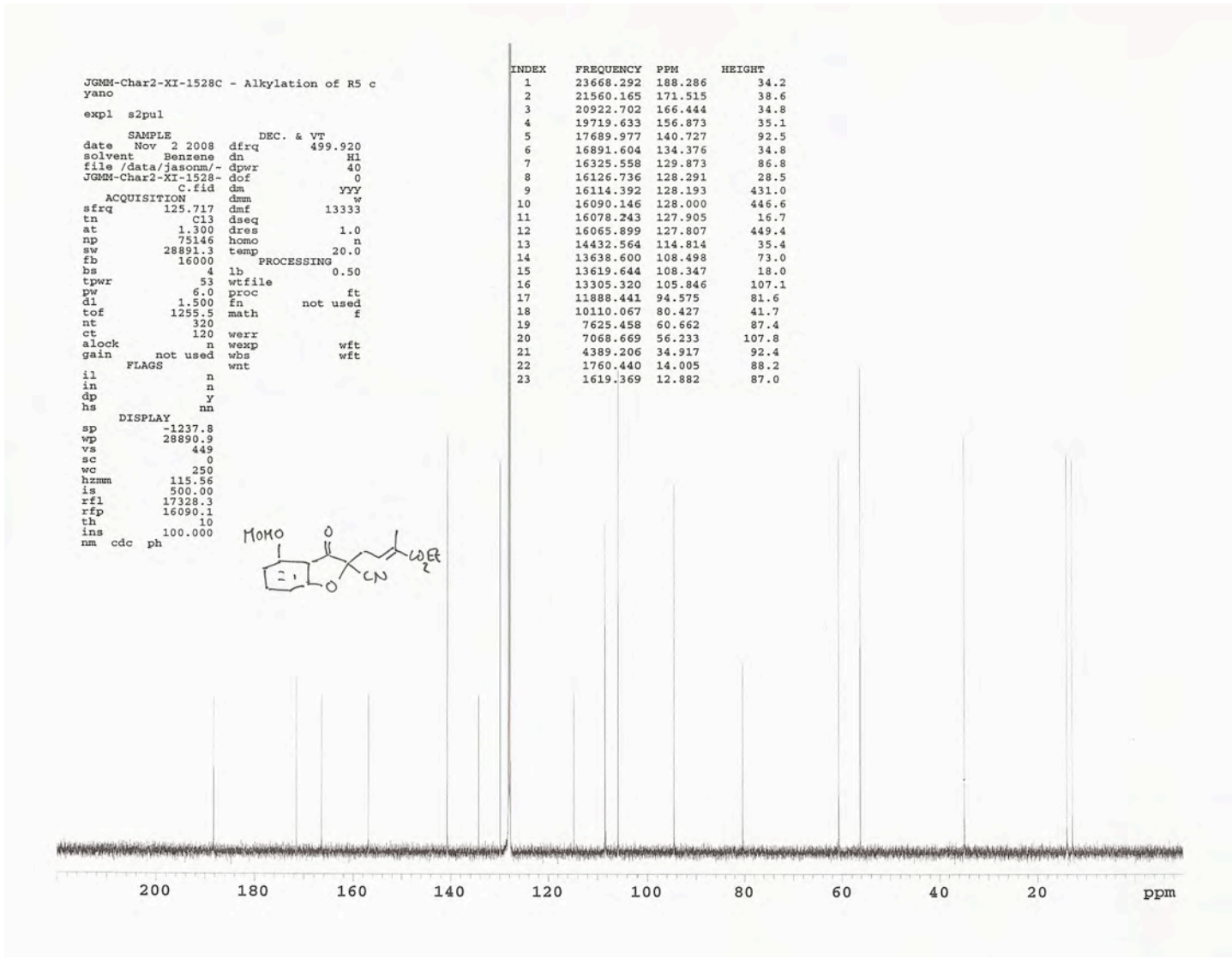
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expl s2pul
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date Nov 2 2008
solvent Benzene
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tof 1255.5
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ct 120
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in n
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6 16891.604 134.376 34.8
7 16325.558 129.873 86.8
8 16126.736 128.291 28.5
9 16114.392 128.193 431.0
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13 14432.564 114.814 35.4
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15 13619.644 108.347 18.0
16 13305.320 105.846 107.1
17 11888.441 94.575 81.6
18 10110.067 80.427 41.7
19 7625.458 60.662 87.4
20 7068.669 56.233 107.8
21 4389.206 34.917 92.4
22 1760.440 14.005 88.2
23 1619.369 12.882 87.0
MOMO
O
CN
O
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160
140
120
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80
60
40
20
ppm

JGMM-Char2-XI-1527 - R5 MOM deprotection

expl s2pul

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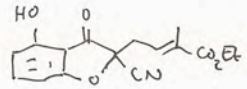

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5	2055.005	6.855	18.3
6	2049.012	6.835	10.4
7	2047.551	6.831	9.8
8	2043.897	6.818	20.2
9	2035.712	6.791	40.9
10	2027.381	6.763	23.0
11	1860.908	6.208	40.1
12	1852.724	6.181	37.2
13	1820.715	6.074	40.6
14	1812.530	6.047	38.0
15	1172.801	3.912	19.1
16	1165.640	3.889	58.9
17	1161.693	3.875	7.7
18	1158.478	3.865	59.9
19	1151.462	3.841	20.4
20	795.716	2.655	10.1
21	788.116	2.629	10.2
22	780.224	2.603	13.6
23	772.623	2.577	13.3
24	693.991	2.315	13.6
25	686.537	2.290	13.7
26	678.498	2.263	10.4
27	671.044	2.239	10.1
28	501.502	1.673	119.4
29	500.918	1.671	118.6
30	496.971	1.658	22.7
31	276.859	0.924	9.2
32	267.797	0.893	60.5
33	260.636	0.869	120.5
34	253.474	0.846	58.5

JGMM-Char2-XI-1527C - R5 MOM deprotectio
n

expl s2pul

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INDEX	FREQUENCY	PPM	HEIGHT
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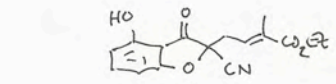
2	12790.227	169.688	25.3
3	12561.058	166.648	24.8
4	11860.072	157.348	35.3
5	10705.337	142.028	43.6
6	10141.164	134.543	32.4
7	9772.027	129.645	48.0
8	9672.501	128.325	309.0
9	9648.121	128.002	309.7
10	9624.028	127.682	310.4
11	8605.246	114.166	25.6
12	8306.667	110.205	46.4
13	8024.437	106.460	21.2
14	7841.733	104.036	50.0
15	6052.841	80.303	33.9
16	4591.209	60.912	41.0
17	2610.722	34.636	51.0
18	1054.153	13.985	48.1
19	971.836	12.893	53.4



JGMM-XI-1512 - NaBH4 red, after tartrate overnight, after column

expl s2pul

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dp	y		
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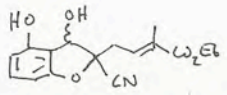

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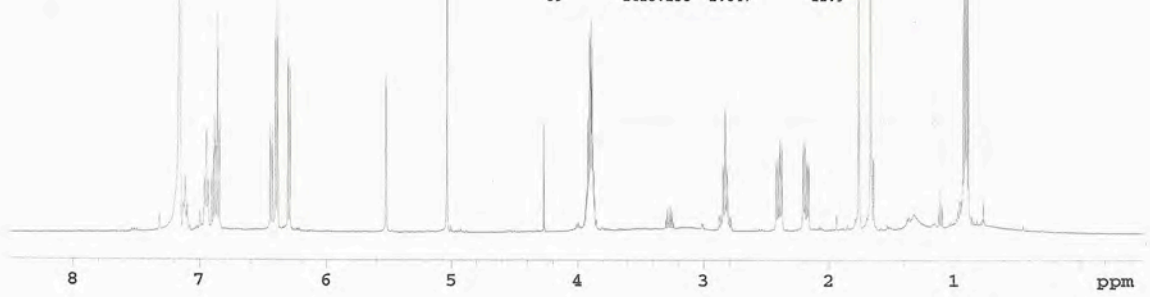
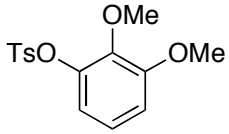
2	3557.435	7.116	10.6	41	1408.021	2.817	12.1
3	3555.970	7.113	11.0	42	1213.197	2.427	13.9
4	3481.752	6.965	10.6	43	1205.384	2.411	14.2
5	3480.287	6.962	10.3	44	1198.060	2.397	17.8
6	3474.427	6.950	19.5	45	1190.248	2.381	17.7
7	3472.962	6.947	19.0	46	1105.287	2.211	16.9
8	3467.103	6.935	10.3	47	1098.451	2.197	17.7
9	3465.638	6.932	9.9	48	1090.150	2.181	13.7
10	3452.943	6.907	11.6	49	1083.314	2.167	13.0
11	3445.130	6.891	22.4	50	879.701	1.760	70.1
12	3438.294	6.878	22.2	51	831.849	1.664	136.2
13	3436.830	6.875	16.2	52	821.107	1.642	14.2
14	3430.482	6.862	42.3	53	554.505	1.109	8.3
15	3422.181	6.845	23.1	54	464.662	0.929	10.8
16	3222.474	6.446	20.9	55	462.220	0.925	41.9
17	3214.173	6.429	20.5	56	455.384	0.911	137.8
18	3201.966	6.405	46.1	57	448.548	0.897	157.0
19	3193.666	6.388	42.7	58	441.224	0.883	70.7
20	3152.162	6.305	33.2				
21	3144.349	6.290	31.6				
22	2763.978	5.529	30.3				
23	2518.373	5.038	68.5				
24	2133.607	4.268	20.6				
25	1963.685	3.928	8.1				
26	1962.220	3.925	7.8				
27	1958.802	3.918	21.9				
28	1956.361	3.913	19.4				
29	1952.943	3.907	38.3				
30	1951.478	3.904	37.3				
31	1949.525	3.900	35.8				
32	1945.619	3.892	40.9				
33	1944.154	3.889	27.8				
34	1942.201	3.885	35.3				
35	1940.248	3.881	12.3				
36	1938.294	3.877	17.1				
37	1935.365	3.871	11.7				
38	1933.412	3.867	7.3				
39	1423.158	2.847	12.9				



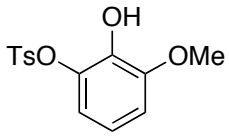
APPENDIX 4

A4.1 Experimental Procedures for Chapter 4

General Information: Commercial reagents were purchased and used without further purification. Toluene, dichloromethane, benzene, and THF were dried over a column of alumina prior to use. Flash chromatography was performed with MP Silitech 32-63D 60Å silica, while thin layer chromatography (TLC) was performed with EMD 250 μm silica gel 60-F_{254} plates. NMRs were acquired on Varian Mercury 300 or Inova 500 or 600 MHz spectrometers and referenced to residual protic solvent. IR spectroscopic information was collected on a Nicolet Avatar 370 OTGS spectrometer. High-resolution mass spectrometry was obtained at the University of Illinois at Urbana-Champaign facility or Cornell University facility.

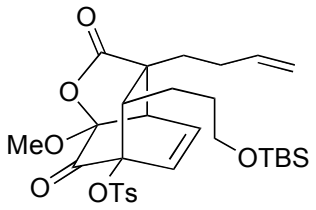


2,3-Dimethoxyphenyl 4-methylbenzenesulfonate (4.10a): In a flask with magnetic stirring was dissolved 2,3-dimethoxyphenol (10 g, 64.9 mmol, 1.0 eq.) in 130 ml CH_2Cl_2. The solution was brought to 0 ^oC and Et_3N (19.9 ml, 143 mmol, 2.2 eq.) then *p*-toluenesulfonyl chloride (13.6 g, 71.3 mmol, 1.1 eq.) were sequentially added. The reaction mixture was stirred for 1.5 h, then washed sequentially with two 100 ml portions 1 M aq. HCl and one 100 ml portion brine. The organic layer was dried with Na_2SO_4, concentrated *in vacuo*, and filtered through a plug of silica with additional CH_2Cl_2. Concentration *in vacuo* gave the tosylated product (19.6 g, 98% yield) as a white solid which was used in the next step without further purification.).



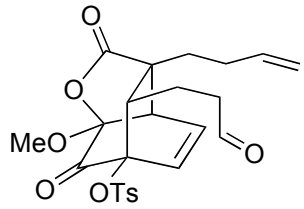
2-Hydroxy-3-methoxyphenyl 4-methylbenzenesulfonate (4.10): In a flame-dried flask under N_2 atmosphere was dissolved the sulfonate **4.10a** (10 g, 32.4 mmol, 1.0 eq.) in 160 ml anhydrous CH_2Cl_2. To this was added $AlCl_3$ (4.32 g, 32.4 mmol, 1.0 eq.) and the reaction mixure brought to 45 ^oC. After 20 h, the reaction mixture was brought to 0 ^oC and acidified with 1M HCl. The organic layer was separated with CH_2Cl_2 (x3) and dried with Na_2SO_4. Recrystallization from CH_2Cl_2/hexanes gave the product phenol (7.03 g, 74% yield) as white crystals. (The chemoselectivity of deprotection was confirmed by sulfonylation of the product with TsCl, yielding a non-symmetrical product. ^1H NMR (400 MHz, C_6D_6) δ 7.83 (d, J = 8.3, 2H), 6.98 (dd, J =

1.2, 8.5, 1H), 6.60 (d, *J* = 8.0, 2H), 6.42 (t, *J* = 8.3, 1H), 6.10 (dd, *J* = 1.3, 8.3, 1H), 5.21 (s, 1H), 2.90 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 148.1, 145.3, 138.7, 136.5, 132.6, 129.6, 128.5, 119.0, 115.8, 109.5, 56.3, 21.7; FTIR (thin film, KCl) 3464, 2959, 2844, 1598, 1618, 1503, 1479, 1443, 1370, 1283, 1174, 1068, 985, 933, 789, 660, 553 cm^{-1}.



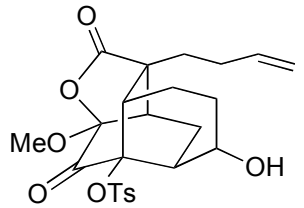
Bicycle 4.19: In a flame-dried flask under N_2 atmosphere with magnetic stirring was dissolved $Pb(OAc)_4$ (213 mg, 0.481 mmol, 1.0 eq.) in 10 ml anhydrous CH_2Cl_2. Diphenic acid (**4.18**) (117 mg, 0.481 mmol, 1.0 eq.) was added, then the acid **4.17** (287 mg, 0.962 mmol, 2.0 eq.). The reaction mixture was stirred for 15 min, then the solvent was removed *in vacuo* on a rotary evaporator purged with N_2. Toluene (10 ml) was added and the solvent again removed *in vacuo*, then this was repeated again in order to remove all residual acetic acid. To this solid was then added 10 ml anhydrous CH_2Cl_2 and it was brought to 0 ºC. Solid **4.13** (142 mg, 0.481 mmol, 1.0 eq.) was added and the reaction stirred 25 min, then brought to ambient temperature for 1 h. The reaction mixture was then filtered through Celite with additional CH_2Cl_2 to give a yellow solution. The solvent was removed *in vacuo* and column chromatography employed (SiO_2; 5% AcOH/10% EtOAc/ 75% hexanes then 20% EtOAc/Hex) to provide the desired ketal (90.5 mg, 32% yield) and 145 mg recovered acid **4.17** (66% total consumption or recovery of acid **4.17**).

The oxidative dearomatization product above was taken up in 15 ml anhydrous PhMe under N_2 atmosphere in a SurfaSil coated flask with magnetic stirring and heated at 80 ºC for 24 h. Removal of the solvent *in vacuo* and crude ^{1}H-NMR indicates a 1:0.25 ratio between the desired bicycle **4.19** and the [3,3] rearrangement product. Column chromatography (SiO_2; 20 → 30% EtOAc/Hex) then provided the bicycle **4.19** (284 mg, 59% yield) as slightly yellow oil. ^{1}H NMR (500 MHz, C_6D_6) δ 8.22 (d, *J* = 8.3, 2H), 6.77 (d, *J* = 8.1, 2H), 6.58 (d, *J* = 8.8, 1H), 5.64 (ddt, *J* = 6.3, 10.0, 16.8, 1H), 5.41 (dd, *J* = 6.8, 8.8, 1H), 5.07 – 4.85 (m, 2H), 3.55 (s, 3H), 3.43 – 3.33 (m, 3H), 3.10 (dd, *J* = 6.8, 1H), 2.76 – 2.60 (m, 1H), 2.20 – 2.06 (m, 1H), 2.06 – 1.91 (m, 1H), 1.81 (s, 3H), 1.80 – 1.69 (m, 1H), 1.59 – 1.45 (m, 3H), 1.41 – 1.28 (m, 2H), 0.97 (s, 9H), 0.04 (d, *J* = 3.9, 6H); ^{13}C NMR (126 MHz, C_6D_6) δ 192.9, 174.4, 144.9, 137.4, 135.6, 131.7, 129.6, 128.8, 126.4, 115.6, 96.7, 92.5, 62.8, 54.5, 53.8, 50.8, 46.1, 33.5, 29.6, 28.2, 26.2, 22.3, 21.1, 18.4, -5.3; FTIR (thin film, KCl) 3074, 2954, 2928, 2855, 1787, 1580, 1253, 1180, 1090, 1041, 949, 903, 836, 776, 559 cm^{-1}.



Bicycle 4.20: In a polypropylene Eppendorf tube with magnetic stirring was dissolved **4.19** (30.5 mg, 0.0516 mmol, 1.0 eq.) in 0.5 ml THF at 0 ºC. To this was added HF-pyridine (5 drops), and the reaction mixture was stirred 15 min, then brought to ambient temperature. Reaction completion was monitored by thin layer chromatography (~2 h), after which the reaction mixture was again brought to 0 ºC and a solution of sat. $NaHCO_3$ carefully added. Water was added and the reaction mixture separated with EtOAc (x4). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 20 → 30 → 40% EtOAc/hexanes) then yielded the free alcohol substrate (17.0 mg, 69% yield).

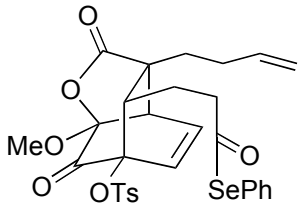
In a flame-dried flask under N_2 atmosphere with magnetic stirring was dissolved oxalyl chloride (4.7 μl, 53.5 μmol, 1.5 eq.) in 0.36 ml anhydrous CH_2Cl_2. The solution was brought to –78 ºC and DMSO (7.6 μl, 107 μmol, 3.0 eq.) was added. After ten minutes, a solution of the alcohol generated above in 0.36 ml anhydrous CH_2Cl_2 was added to the reaction mixture. After another 10 min, Et_3N (25 μl, 179 μmol, 5.0 eq.) was added and the reaction mixture brought to ambient temperature. The reaction was then quenched with sat. NH_4Cl and separated with CH_2Cl_2 (x3). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 30% EtOAc/hexanes) then provided the aldehyde **4.20** (13.8 mg, 81% yield) as a slightly yellow oil. ^{1}H NMR (500 MHz, C_6D_6) δ 9.11 (s, 1H), 8.17 (d, *J* = 8.5, 2H), 6.76 (d, *J* = 8.1, 2H), 6.38 (d, *J* = 8.5, 1H), 5.56 (ddt, *J* = 6.3, 10.3, 16.8, 1H), 5.35 (dd, *J* = 6.8, 8.5, 1H), 4.97 – 4.89 (m, 2H), 3.52 (s, 3H), 3.04 (dd, *J* = 1.5, 6.8, 1H), 2.56 – 2.51 (m, 1H), 2.24 – 2.06 (m, 1H), 1.96 – 1.74 (m, 4H), 1.85 (s, 3H), 1.72 – 1.60 (m, 1H), 1.57 – 1.43 (m, 1H), 1.11 (ddd, *J* = 5.2, 10.3, 13.7, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ 198.9, 192.5, 174.2, 145.1, 137.2, 135.3, 131.5, 129.7, 128.7, 126.7, 115.8, 96.8, 92.4, 54.6, 53.7, 50.2, 45.8, 44.0, 29.5, 27.9, 21.1, 17.5; FTIR (thin film, KCl) 3075, 2955, 2924, 2851, 2731, 1787, 1760, 1724, 1642, 1451, 1367, 1248, 1179, 1090, 1040, 945, 904, 818, 750, 682, 559 cm^{-1}.



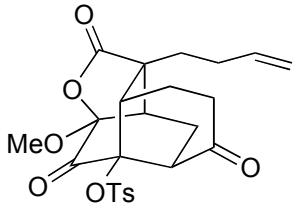
Bicycle 4.21: In a flame-dried flask with mechanical stirring was suspended freshly filed samarium metal (21.5 mg, 0.143 mmol) in 1.1 ml anhydrous THF. To this was added 1,2-diiodoethane (30.2 mg, 0.107 mmol), which after 15 min resulted in a deep blue solution color. After an additional 15 min, HMPA (93 μl, 0.536 mmol;

previously sparged with N_2) was added and the solution color became a deep purple.

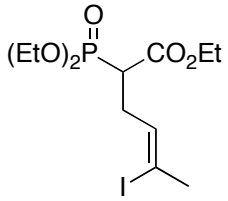
In a separate flame-dried flask under N_2 atmosphere with mechanical stirring was dissolved the aldehyde **4.20** (0.5 mg, 1.05 μmol) in 0.1 ml anhydrous THF. This solution was brought to –78 °C and portions of the SmI_2/HMPA solution prepared above were added drop by drop until all stating material was seen to be consumed by TLC. At this time 2 drops *t*-BuOH were added and the reaction mixture brought to ambient temperature. An aqueous solution of 20 wt% Rochelle salt was then added the biphasic mixture stirred vigorously for 30 min. EtOAc was added, and the organic layer separated (x3). The combined organic layers were dried over Na_2SO_4 and concentrate *in vacuo*. Column chromatography (50% EtOAc/Hex) then provided the monocyclized alcohol **4.21** as a white film. ^{1}H NMR (600 MHz, C_6D_6) δ 8.16 (d, *J* = 8.39, 2H), 6.78 (d, *J* = 8.25, 2H), 5.67 – 5.59 (m, 1H), 4.98 – 4.91 (m, 2H), 3.78 – 3.71 (m, 1H), 3.63 (s, 3H), 3.25 (dt, *J* = 2.12, 4.38, 1H), 2.35 (t, *J* = 2.98, 1H), 2.09 – 2.01 (m, 1H), 1.96 – 1.94 (m, 2H), 1.94 – 1.92 (m, 1H), 1.80 (s, 3H), 1.71 – 1.64 (m, 1H), 1.62 (ddd, *J* = 2.60, 11.36, 15.74), 1.56 – 1.51 (m, 1H), 1.43 (ddd, *J* = 5.54, 11.00, 14.64, 1H), 1.36 – 1.32 (m, 1H), 1.31 – 1.26 (m, 1H), 1.04 (ddd, *J* = 4.86, 14.23, 25.45, 1H). Confirmed by gCOSY and HSQCAD NMR experiments. FTIR (thin film, KCl) 2954, 2917, 2850, 1772, 1734, 1463, 1248, 1176, 1096, 985, 895, 815, 680, 548 cm^{-1}.



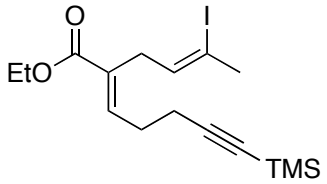
Bicycle 4.22: In a flame-dried flask under N_2 atmosphere with mechanical stirring was dissolved **4.20** (9.2 mg, 19.4 μmol, 1.0 eq.) and 2-methyl-2-butene (0.1 ml) in 0.2 ml *t*-BuOH. To this was added a solution of sodium chlorite (17.5 mg, 0.194 mmol, 10 eq.) and NaH_2PO_4 (18.7 mg, 0.136 mmol, 7 eq.) in 0.2 ml H_2O. The reaction mixture was allowed to stir for 1.5 h, then separated with EtOAc (x4). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo* to give a clear oil which was used without further purification. ^{1}H NMR (500 MHz, Benzene) δ 8.19 (d, *J* = 8.3, 2H), 7.56 – 7.40 (m, 2H), 7.06 – 6.98 (m, 3H), 6.77 (d, *J* = 7.8, 2H), 6.44 (dt, *J* = 1.5, 8.8, 1H), 5.53 (ddt, *J* = 6.5, 10.3, 16.8, 1H), 5.32 (dd, *J* = 6.8, 8.8, 1H), 5.01 – 4.82 (m, 2H), 3.52 (s, 3H), 3.02 (dd, *J* = 1.5, 6.8, 1H), 2.73 (ddd, *J* = 5.6, 10.7, 16.4, 1H), 2.47 (t, *J* = 5.4, 1H), 2.41 (ddd, *J* = 4.9, 11.0, 16.3, 1H), 1.95 (dtd, *J* = 5.4, 10.7, 16.4, 1H), 1.91 – 1.82 (m, 2H), 1.81 (s, 3H), 1.71 – 1.58 (m, 2H), 1.11 (ddd, *J* = 5.2, 11.1, 13.7, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ 197.7, 192.3, 173.8, 145.1, 137.0, 136.0, 135.2, 131.2, 129.7, 129.4, 128.8, 128.7, 126.8, 126.7, 115.7, 96.6, 92.0, 54.5, 53.4, 49.4, 47.2, 45.8, 29.4, 27.9, 21.1, 21.0; FTIR (thin film, KCl) 3073, 2955, 2919, 2850, 1787, 1724, 1597, 1548, 1350, 1247, 1179, 1090, 1043, 946, 901, 742, 610, 558 cm^{-1}.



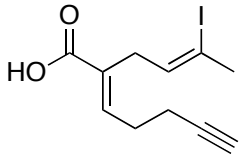
Bicycle 4.23: In a flame-dried flask under N_2 atmosphere with mechanical stirring was dissolved acyl selenide **4.22** (2.4 mg, 3.81 μmol, 1.0 eq.) in 0.2 ml anhydrous PhH. A solution of *n*-Bu_3SnH (1.31 μl, 4.96 μmol, 1.3 eq.) and AIBN (0.13 mg, 0.76 μmol, 0.2 eq.) was added and the reaction mixture brought to 80 ºC. After 1 h, an additional 1.3 eq. *n*-Bu_3SnH and 0.2 eq. AIBN was added and the reaction mixture was stirred for an additional hour. The solvent was then stripped *in vacuo* and the crude reaction product subjected to preparative TLC (SiO_2; 30% EtOAc/Hex) to provide the ketone **4.23** (1.3 mg, 72% yield) along with 0.5 mg of the aldehyde **4.20**.



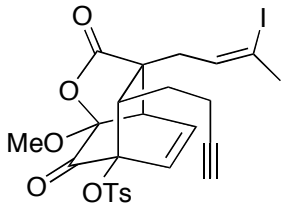
(*Z*)-Ethyl 2-(diethoxyphosphoryl)-5-iodohex-4-enoate (4.25): In a flame-dried flask under N_2 atmosphere with magnetic stirring was washed NaH (820 mg of a 60% dispersion in oil, 20.4 mmol, 1.1 eq.) with two portions hexanes. To this was added 10 ml anhydrous THF and the suspension brought to 0 ºC. Triethylphosphonoacetate (4.16 g, 18.5 ml, 1.0 eq.) was added slowly with venting and stirred 30 min. Allylic bromide **4.24** was then added and the reaction mixture brought to ambient temperature and stirred in the dark. After 1 h the solution was too viscous to stir efficiently, so an additional 10 ml anhydrous THF was added, and the reaction mixture stirred an additional 2 h. A solution of sat. NH_4Cl was added, and the organic layer separated with EtOAc (x3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 50 → 65% EtOAc/hexanes) provided the phosphonate **4.25** (3.65 g, 49% yield) as a yellow oil. ^{1}H NMR (300 MHz, C_6D_6) δ 5.41 (t, *J* = 6.5, 1H), 4.17 – 3.79 (m, 6H), 3.19 (dddd, *J* = 1.0, 4.6, 10.2, 21.9, 1H), 3.11 – 2.93 (m, 1H), 2.92 – 2.76 (m, 1H), 2.13 (s, 3H), 1.13 – 0.91 (m, 9H); ^{13}C NMR (75 MHz, C_6D_6 , ^{13}C – ^{31}P coupling observed) δ 168.6 (d, *J* = 4.9), 132.4 (d, *J* = 14.6), 103.5, 62.6 (d, *J* = 6.2) 62.4 (d, *J* = 6.6), 61.3, 45.3 (d, *J* = 129.6), 34.9 (d, *J* = 4.2), 33.4, 16.4 (d, *J* = 5.7, 14.10); FTIR (thin film, KCl) 2982, 2913, 1730, 1430, 1368, 1368, 1324, 1257, 1163, 1098, 1024, 969, 857, 792, 579, 496 cm^{-1}.



(*E*)-Ethyl 2-((*Z*)-3-iodobut-2-enyl)-7-(trimethylsilyl)hept-2-en-6-ynoate (4.27): In a flame-dried flask under N_2 atmosphere with magnetic stirring was dissolved phosphonate **4.25** (2.1 g, 5.20 mmol, 1.2 eq.) in 22 ml anhydrous PhMe. The solution was brought to 0 ^oC and *t*-BuOK (583 mg, 5.20 mmol, 1.2 eq.) was added. The reaction mixture became yellow, was stirred for 1 h, then brought to –78 ^oC. In a separate flame-dried flask under N_2 atmosphere was dissolved aldehyde **4.26** (670 mg, 4.33 mmol, 1.0 eq.) in 22 ml dry PhMe. A canula was used to slowly add this solution down the side of the reaction flask into the phosphonate solution over 30 min. The reaction was allowed to stir in the dark at –78 ^oC for 3 h after the addition, then brought out of the cooling bath to warm to ambient temperature. A solution of sat. NH_4Cl was then added and the reaction mixture separated with EtOAc (x3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 5% Et_2O/pentane) afforded **4.27** (940 mg, 54% yield) as a yellow oil. ^1H NMR (300 MHz, C6D6) δ 6.90 (t, *J* = 7.5, 1H), 5.34 (td, *J* = 1.5, 6.4, 1H), 4.01 (q, *J* = 7.2, 2H), 3.16 (d, *J* = 6.3, 2H), 2.23 (dd, *J* = 7.2, 14.3, 2H), 2.17 (d, *J* = 1.5, 3H), 2.05 (t, *J* = 7.2, 2H), 1.00 (t, *J* = 7.1, 3H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, C6D6) δ 166.7, 141.4, 133.5, 131.3, 106.2, 101.1, 85.8, 60.5, 35.5, 33.5, 28.3, 19.5, 14.4, 0.26; FTIR (thin film, KCl) 2958, 2915, 2176, 1710, 1649, 1428, 1371, 1279, 1249, 1201, 1094, 1054, 914, 842, 759, 638 cm^{-1}.

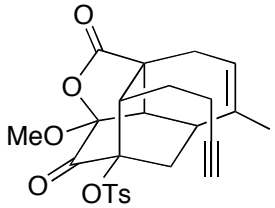


(*E*)-2-((*Z*)-3-iodobut-2-enyl)hept-2-en-6-ynoic acid (4.28): In a flask with magnetic stirring was dissolved ester **4.27** (247 mg, 0.618 mmol, 1.0 eq.) in 1.9 ml EtOH and 0.6 ml H_2O. Lithium hydroxide (76.8 mg, 1.85 mmol, 3.0 eq.) was added and the solution brought to 50 ºC. The reaction mixture was allowed to stir in the dark for 2 h, then brought to 0 ºC and 1 M aq. HCl (1.85 ml, 1.85 mmol, 3.0 eq.) was added. The organic layer was separated with EtOAc (x3) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo* to provide the acid **4.28** (151 mg, 74% yield) which was used without further purification.



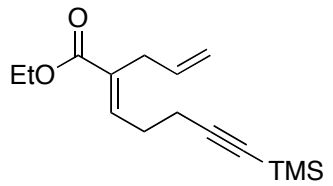
Bicycle 4.29: In a flame-dried flask under N_2 atmosphere with magnetic stirring was dissolved $Pb(OAc)_4$ (497 mg, 1.12 mmol, 1.1 eq.) in 10 ml anhydrous CH_2Cl_2. Diphenic acid (**4.18**) (272 mg, 1.12 mmol, 1.1 eq.) was added, then the acid **4.28** (300 mg, 1.02 mmol, 2.2 eq.). The reaction mixture was stirred for 30 min, then the solvent was removed *in vacuo* on a rotary evaporator purged with N_2. Toluene (10 ml) was added and the solvent again removed *in vacuo*, then this was repeated again in order to remove all residual acetic acid. To this solid was then added 10 ml anhydrous CH_2Cl_2 and it was brought to 0 ºC. Solid **4.13** (300 mg, 1.02 mmol, 1.0 eq.) was added and the reaction stirred 25 min, then brought to ambient temperature for 30 min. The reaction mixture was then filtered through Celite with additional CH_2Cl_2 to give a yellow solution. The solvent was removed *in vacuo* and column chromatography employed (SiO_2; 5% AcOH/10% EtOAc/ 75% hexanes) to provide the desired ketal (306 mg, 55% yield) and 382 mg recovered acid **4.28**.

The oxidative dearomatization product above (36 mg, 60.4 μmol) was taken up in 6 ml anhydrous PhMe under N_2 atmosphere in a SurfaSil coated flask with magnetic stirring and heated at 75 ºC for 9 h, then 90 ºC for an additional 5 h. Removal of the solvent *in vacuo* and column chromatography (SiO_2; 20 → 30% EtOAc/Hex) then provided the bicycle **4.29** (17.4 mg, 48% yield) as a yellow oil. ^{1}H NMR (500 MHz, C_6D_6) δ 8.14 (d, *J* = 8.4, 2H), 6.74 (d, *J* = 8.0, 2H), 6.61 (d, *J* = 8.8, 1H), 5.87 (dd, *J* = 6.8, 8.5, 1H), 5.29 (dd, *J* = 5.0, 8.4, 1H), 3.52 (s, 3H), 3.21 (d, *J* = 6.8, 1H), 2.70 (t, *J* = 5.5, 1H), 2.57 (dd, *J* = 3.9, 13.9, 1H), 2.31 – 2.01 (m, 2H), 2.10 (dd, *J* = 9.5, 13.6, 2H), 2.02 (s, 3H), 1.97 – 1.85 (m, 1H), 1.81 (s, 3H), 1.69 (t, *J* = 2.5, 1H), 1.49 (dq, *J* = 6.4, 8.8, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ 192.6, 173.8, 145.0, 135.3, 131.2, 129.9, 129.7, 128.7, 127.9, 108.1, 97.1, 91.9, 82.8, 70.3, 54.8, 52.8, 48.9, 47.0, 37.2, 33.5, 24.9, 21.1, 18.9; FTIR (thin film, KCl) 3294, 3073, 2955, 2918, 2851, 1788, 1739, 1550, 1353, 1244, 1179, 1090, 948, 901, 817, 767, 683, 557 cm^{-1}.

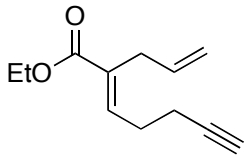


Bicycle 4.30: In a flame-dried flask under N_2 atmosphere with mechanical stirring was dissolved **4.29** (1.6 mg, 2.68 μmol, 1.0 eq.) in 0.2 ml anhydrous THF. The solution was brought to –78 ºC and *n*-Bu_3SnH (17 μl of a stock solution of 0.05 ml *n*-Bu_3SnH in 0.95 ml anhydrous THF, 3.22 μmol, 1.2 eq.) and Et_3B (0.5 μl of a 1.0 M solution in THF, 0.54 μmol, 0.2 eq.) were added. Over this reaction mixture was

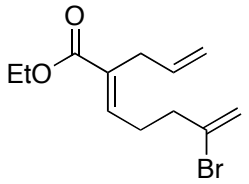
injected 0.1 ml ambient air in order to initiate the Et_3B. After 45 min, the reaction mixture was brought to 0 °C and allowed to stir an additional 1.5 h. The solvent was then removed *in vacuo* and the crude residue subjected to column chromatography (SiO_2; 10 → 20 → 30% EtOAc/Hex) to provide the monocyclized product **4.30** as a white solid. ^{1}H NMR (600 MHz, C_6D_6) δ 8.13 (d, *J* = 8.30, 2H), 6.74 (d, *J* = 7.98, 2H), 4.75 (dd, *J* = 1.51, 3.27, 1H), 3.61 (s, 3H), 2.58 (ddd, *J* = 2.19, 11.35, 13.67, 1H) 2.45 (dt, *J* = 2.22, 8.03, 1H), 2.19 – 2.17 (m, 1H), 2.13 (ddd, *J* = 1.33, 4.90, 18.27, 1H), 2.09 – 2.03 (m, 1H), 2.00 (dd, *J* = 1.92, 13.91, 1H), 1.98 – 1.93 (m, 1H), 1.94-1.88 (m, 1H), 1.93 (d, *J* = 3.56, 1H), 1.80 (s, 3H), 1.70 (t, *J* = 2.56, 1H), 1.09 (s, 3H). Confirmed by gCOSY and HSQC NMR experiments. FTIR (thin film, KCl) 3284, 2950, 2917, 2849, 1793, 1773, 1457, 1350, 1267, 1233, 1190, 1178, 1100, 1041, 987, 889, 753, 559 cm^{-1}.



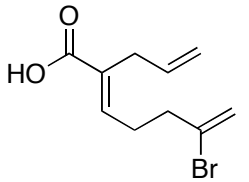
(*E*)-ethyl 2-allyl-7-(trimethylsilyl)hept-2-en-6-ynoate (4.32): In a flame-dried flask under N_2 atmosphere with magnetic stirring was dissolved phosphonate **4.31** (4.9 g, 18.5 mmol, 1.6 eq.) in 40 ml anhydrous PhMe. The solution was brought to 0 °C and *t*-BuOK (1.8 g, 16.1 mmol, 1.4 eq.) was added. The reaction mixture was stirred for 1.5 h, then brought to –78 °C. In a separate flame-dried flask under N_2 atmosphere was dissolved aldehyde **4.26** (1.78 g, 11.5 mmol, 1.0 eq.) in 40 ml anhydrous PhMe. A canula was used to slowly add this solution down the side of the reaction flask into the phosphonate solution over 30 min. The reaction was allowed to stir at –78 °C for 1 hr after the addition, then brought out of the cooling bath to warm to ambient temperature over 20 min. A solution of sat. NH_4Cl was added and the reaction mixture separated with EtOAc (x3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 2.5 → 5% Et_2O/pentane) then provided **4.32** (1.66 g) and its *Z* isomer (270 mg) as colorless oils (1.93 g total product, 6.1:1 *E*:*Z*, 64% overall yield). ^{1}H NMR (300 MHz, C_6D_6) δ 6.95 (t, *J* = 7.0, 1H), 5.83 (ddt, *J* = 6.1, 10.1, 16.2, 1H), 4.99 (ddq, *J* = 1.7, 10.1, 21.3, 2H), 4.01 (q, *J* = 7.1, 2H), 3.06 (d, *J* = 6.1, 2H), 2.17 – 1.93 (m, 4H), 0.97 (t, *J* = 7.1, 3H), 0.19 (s, 8H); ^{13}C NMR (75 MHz, C_6D_6) δ 166.6, 140.8, 135.8, 131.6, 115.2, 106.3, 85.5, 60.4, 31.2, 27.8, 19.4, 14.3, 0.18; FTIR (thin film, KCl) 3080, 2979, 2960, 2904, 2177, 1712, 1639, 1432, 1371, 1278, 1210, 1128, 1102, 1055, 996, 913, 844, 760, 699, 639 cm^{-1}.



(*E*)-Ethyl 2-allylhept-2-en-6-ynoate: In a flask with magnetic stirring was dissolved **4.32** (430 mg, 1.63 mmol, 1.0 eq.) in 16 ml THF at 0 ºC. Tetrabutylammonium fluoride hydrate (468 mg, 1.79 mmol, 1.1 eq.) was added and the reaction mixture was stirred for 10 min. The reaction mixture was separated with EtOAc (x3) and the combined organic layers dried with Na_2SO_4 and concentration *in vacuo*. Column chromatography (SiO_2; 5% EtOAc/Hex) provided the free alkyne (279 mg, 89% yield) as a slightly volatile colorless oil which was used directly in the next step.

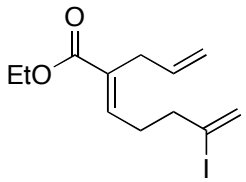


(*E*)-ethyl 2-allyl-6-bromohepta-2,6-dienoate (4.33a): In a flame-dried flask under N_2 atmosphere was dissolved the above free alkyne (*E*)-ethyl 2-allylhept-2-en-6-ynoate (866 mg, 4.50 mmol, 1.0 eq.) in 15 ml anhydrous CH_2Cl_2 with magnetic stirring. The solution was brought to 0 ^oC and a solution of *B*-Br-9-BBN (1.0 M in hexanes; 5.9 ml, 5.85 mmol, 1.3 eq.) was added and the reaction flask covered with foil. After 3 h AcOH (0.77 ml, 13.5 mmol, 3.0 eq.) was added and the reaction mixture stirred 1 h, after which time it was poured into a solution of hydrated sodium perborate in 20 ml H_2O. After 30 min the reaction mixture was separated with CH_2Cl_2 (x3) and the combined organic layers dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 10% EtOAc/Hex) provided the vinyl bromide **4.33a** (1.22 g, 98% yield) as a yellow oil. ^1H NMR (400 MHz, C_6D_6) δ 6.78 (t, *J* = 6.9, 1H), 5.85 (ddt, *J* = 6.2, 10.1, 16.4, 1H), 5.19 (d, *J* = 1.8, 1H), 5.12 (s, 1H), 5.02 (ddd, *J* = 1.6, 11.5, 13.5, 2H), 4.02 (q, *J* = 7.2, 2H), 3.08 (d, *J* = 6.0, 2H), 2.24 – 1.98 (m, 4H), 0.97 (t, *J* = 7.0, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 166.8, 140.6, 135.8, 133.4, 131.7, 117.4, 115.3, 60.5, 40.3, 31.3, 27.1, 14.26; FTIR (thin film, KCl) 3079, 2980, 2930, 2853, 1711, 1647, 1443, 1369, 1278, 1212, 1145, 1115, 1052, 995, 890, 759, 536 cm^{-1}.

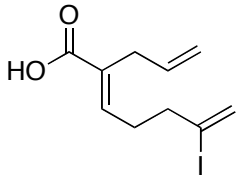


(*E*)-2-Allyl-6-bromohepta-2,6-dienoic acid (4.33): In a flask with magnetic stirring was dissolved ester **4.33a** (1.22 g, 4.47 mmol, 1.0 eq.) in 15 ml EtOH and 5 ml H_2O. To this was added LiOH (562 mg, 13.4 ml, 3.0 eq.) and the reaction mixture brought

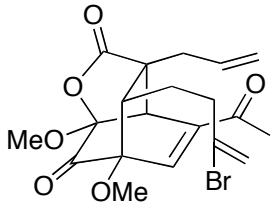
to 50 ºC. After 2 h stirring, the reaction mixture was brought to 0 ºC and 1M aq. HCl (20 ml, 20 mmol, 4.5 eq.) was added. The organic layer was extracted with EtOAc (x3) and the combined organic layers dried with Na_2SO_4 and concentrated *in vacuo* to provide the acid **4.33** which was used without further purification.



(*E*)-Ethyl 2-allyl-6-iodohepta-2,6-dienoate (4.34a): In a flame-dried flask under N_2 atmosphere was dissolved (*E*)-ethyl 2-allylhept-2-en-6-ynoate (200 mg, 1.04 mmol, 1.0 eq.) in 3.5 ml anhydrous CH_2Cl_2 with magnetic stirring. The solution was brought to 0 ^oC and a solution of *B*-I-9-BBN (1.0 M in hexanes; 1.25 ml, 1.25 mmol, 1.2 eq.) was added and the reaction flask covered with foil. After 1.5 h AcOH (0.18 ml, 3.12 mmol, 3.0 eq.) was added and the reaction mixture stirred 1 h, after which time it was poured into a solution of hydrated sodium perborate in 4.8 ml H_2O. After 30 min the reaction mixture was separated with CH_2Cl_2 (x3) and the combined organic layers dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 10% EtOAc/Hex) provided the vinyl iodide **4.34a** (287 mg, 86% yield) as a yellow oil. ^1H NMR (300 MHz, C_6D_6) δ 6.83 – 6.72 (m, 1H), 5.85 (ddt, *J* = 6.1, 10.1, 16.2, 1H), 5.58 (d, *J* = 1.2, 1H), 5.46 (d, *J* = 1.5, 1H), 5.02 (ddq, *J* = 1.6, 10.1, 25.6, 2H), 4.01 (q, *J* = 7.1, 2H), 3.09 (d, *J* = 6.1, 2H), 2.23 – 1.98 (m, 4H), 0.97 (t, *J* = 7.1, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 166.7, 140.4, 135.8, 131.7, 126.2, 115.3, 110.76, 60.5, 44.2, 31.4, 28.3, 14.3; FTIR (thin film, KCl) 3078, 2979, 2930, 2905, 1711, 1648, 1617, 1443, 1369, 1277, 1211, 1140, 1113, 1052, 994, 900, 759 cm^{-1}.

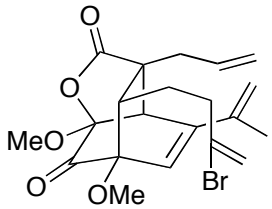


(*E*)-2-Allyl-6-iodohepta-2,6-dienoic acid (4.34): In a flask with magnetic stirring was dissolved ester **4.34a** (1.11 g, 3.47 mmol, 1.0 eq.) in 10.5 ml EtOH and 3.5 ml H_2O. The solution was brought to 50 ºC and a solution of LiOH (174 mg, 4.16 mmol, 1.2 eq.) in 4.2 ml H_2O was slowly added via syringe pump over 4 h. After an additional 8 h stirring, the reaction mixture was brought to 0 ºC and 1M aq. HCl (4.16 ml, 4.16 mmol, 1.2 eq.) was added. The organic layer was extracted with EtOAc (x3) and the combined organic layers dried with Na_2SO_4 and concentrated *in vacuo* to provide the acid **4.34** which was used without further purification.



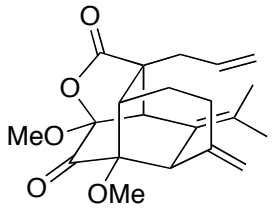
Vinyl Bromide Bicycle 4.36: In a flame-dried flask under N_2 atmosphere with magnetic stirring was dissolved $Pb(OAc)_4$ (1.0 g, 2.26 mmol, 1.0 eq.) in 45 ml anhydrous CH_2Cl_2. Diphenic acid (**4.18**) (548 mg, 2.26 mmol, 1.0 eq.) was added, then the acid **4.33** (1.11 g, 4.53 mmol, 2.0 eq.). The reaction mixture was stirred for 20 min, then the solvent was removed *in vacuo* on a rotary evaporator purged with N_2. Toluene (50 ml) was added and the solvent again removed *in vacuo*, then this was repeated again in order to remove all residual acetic acid. To this solid was then added 45 ml anhydrous CH_2Cl_2 and it was brought to 0 ºC. Solid 3',5'-dimethoxy-4'-hydroxyacetophenone (**4.35**) (489 mg, 2.49 mmol, 1.1 eq.) was added and the reaction stirred 25 min, then brought to ambient temperature for 1 h. The reaction mixture was then filtered through Celite with additional CH_2Cl_2 to give a yellow solution. The solvent was removed *in vacuo* and column chromatography employed (SiO_2; 5% Et_3N/20% EtOAc/ 75% hexanes) to provide the desired ketal (475 mg, 48% yield).

The oxidative dearomatization product above was taken up in 22 ml anhydrous PhMe under N_2 atmosphere in a SurfaSil coated flask with magnetic stirring and heated at 90 ºC for 7 h. Removal of the solvent *in vacuo* and column chromatography (SiO_2; 20 → 30% EtOAc/Hex) provided the bicycle **4.36** (284 mg, 60% yield) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 6.44 (dd, *J* = 1.0, 2.0, 1H), 5.88 (dddd, *J* = 5.6, 8.8, 10.0, 17.1, 1H), 5.30 – 5.11 (m, 4H), 4.51 (d, *J* = 2.2, 1H), 3.36 (s, 3H), 3.20 (s, 3H), 2.69 (dd, *J* = 5.7, 13.6, 1H), 2.49 (dd, *J* = 2.4, 8.5, 1H), 2.25 – 2.07 (m, 2H), 1.84 – 1.76 (m, 1H), 1.73 (dd, *J* = 8.9, 13.6, 1H), 1.56 (s, 3H), 1.19 (dtd, *J* = 5.4, 8.8, 14.4, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ 195.5, 192.6, 174.4, 141.0, 138.8, 133.2, 131.7, 122.2, 118.2, 97.7, 87.7, 54.0, 53.3, 52.8, 46.2, 41.8, 41.7, 33.7, 24.1, 23.5; FTIR (thin film, KCl) 3080, 2978, 2944, 2848, 1790, 1759, 1678, 1628, 1444, 1261, 1239, 1180, 1054, 942 885, 593 cm^{-1}.

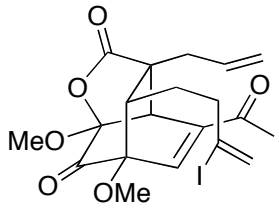


Vinyl Bromide Bicycle 4.37: In a flame-dried flask under N_2 atmosphere with magnetic stirring was dissolved methyltriphenylphosphonium bromide (100 mg, 0.28 mmol) in 0.72 ml anhydrous THF. The solution was brought to –78 ºC and *n*-BuLi (1.53 M in pentanes, 0.17 ml, 0.27 mmol) slowly added. The resultant yellow solution was stirred for 15 min, then brought to 0 ºC. In a separate flame-dried flask under N_2

atmosphere with magnetic stirring was dissolved bicycle **4.36** (37 mg, 84.2 μmol, 1.0 eq.) in 0.85 ml anhydrous THF at –78 ºC. To this was added the prepared phosphonium ylide (0.29 ml of the 0.3 M soln., 88.4 μmol, 1.05 eq.) and the reaction mixture became red. The solution was allowed to stir for 15 min, then brought to 0 ºC and stirred an additional 20 min. After this time a solution of sat. NH_4Cl was added, then brine, and the organic layer separated with EtOAc (x3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; 20% EtOAc/Hex) provided the desired **4.37** (17.8 mg, 48% yield) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 5.93 (d, *J* = 1.5, 1H), 5.79 (dtd, *J* = 4.5, 10.0, 17.1, 1H), 5.18 (s, 2H), 5.09 (s, 1H), 5.02 – 4.92 (m, 2H), 4.80 (s, 1H), 3.80 (d, *J* = 2.4, 1H), 3.53 (s, 3H), 3.26 (s, 3H), 2.79 (ddt, *J* = 1.6, 4.2, 13.7, 1H), 2.50 (ddd, *J* = 1.0, 3.5, 7.8, 1H), 2.26 – 2.15 (m, 2H), 1.92 – 1.83 (m, 1H), 1.85 (dd, *J* = 9.6, 13.8, 1H), 1.47 (d, *J* = 0.7, 3H), 1.34 (dtd, *J* = 6.3, 8.3, 14.4, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ 196.5, 175.0, 139.3, 139.1, 133.6, 133.2, 126.6, 120.9, 117.9, 114.8, 98.2, 87.5, 54.2, 53.8, 53.1, 46.2, 45.7, 41.7, 34.1, 23.5, 19.6; FTIR (thin film, KCl) 3092, 2950, 2925, 2849, 1789, 1755, 1629, 1595, 1445, 1330, 1296, 1248, 1170, 1057, 933, 892, 682, 536 cm^{-1}.

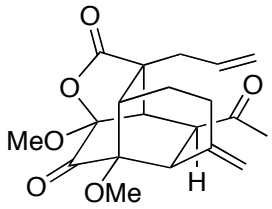


Bicycle 4.38: In a flame-dried flask under N_2 atmosphere with magnetic stirring was dissolved the triene **4.37** (1.4 mg, 3.2 μmol, 1.0 eq.) in 0.32 ml anhydrous PhH at 50 ºC. A solution of *n*-Bu_3SnH (1.0 μl, 3.8 μmol, 1.2 eq.) and AIBN (0.10 mg, 0.64 μmol, 0.2 eq.) in 0.05 ml anhydrous PhH was added and the reaction mixture stirred for 2.5 h. The solvent was then stripped *in vacuo* and the resultant oil subjected to column chromatography (SiO_2; 10 → 20 → 30% EtOAc/Hex), providing **4.38** (1.0 mg, 91% yield). ^{1}H NMR (600 MHz, C_6D_6) δ 5.86 (dtd, *J* = 4.6, 10.0, 17.1, 1H), 5.02 (dd, *J* = 13.6, 19.4, 2H), 4.82 (t, *J* = 1.7, 1H), 4.67 (s, 1H), 3.63 (s, 1H), 3.60 (s, 3H), 3.32 (s, 1H), 3.08 (s, 3H), 2.84 (dd, *J* = 4.5, 13.8, 1H), 2.44 – 2.34 (m, 1H), 2.14 (dd, *J* = 9.9, 13.6, 1H), 1.94 (td, *J* = 5.1, 13.9, 1H), 1.74 (dd, *J* = 5.0, 13.8, 1H), 1.52 (d, *J* = 1.6, 3H), 1.51 – 1.42 (m, 1H), 1.35 (d, *J* = 1.0, 3H), 1.30 – 1.26 (m, 1H); ^{13}C NMR (determined by HSQCAD, gHMBCAD) δ 202.0, 175.3, 142.9, 137.5, 133.9, 120.8, 119.9, 113.0, 103.0, 83.6, 53.9, 52.9, 51.6, 50.7, 46.8, 35.4, 33.4, 28.3, 22.6, 21.1, 21.0; FTIR (thin film, KCl) 2907, 2849, 1787, 1756, 1588, 1443, 1310, 1242, 1080, 927 cm^{-1}.



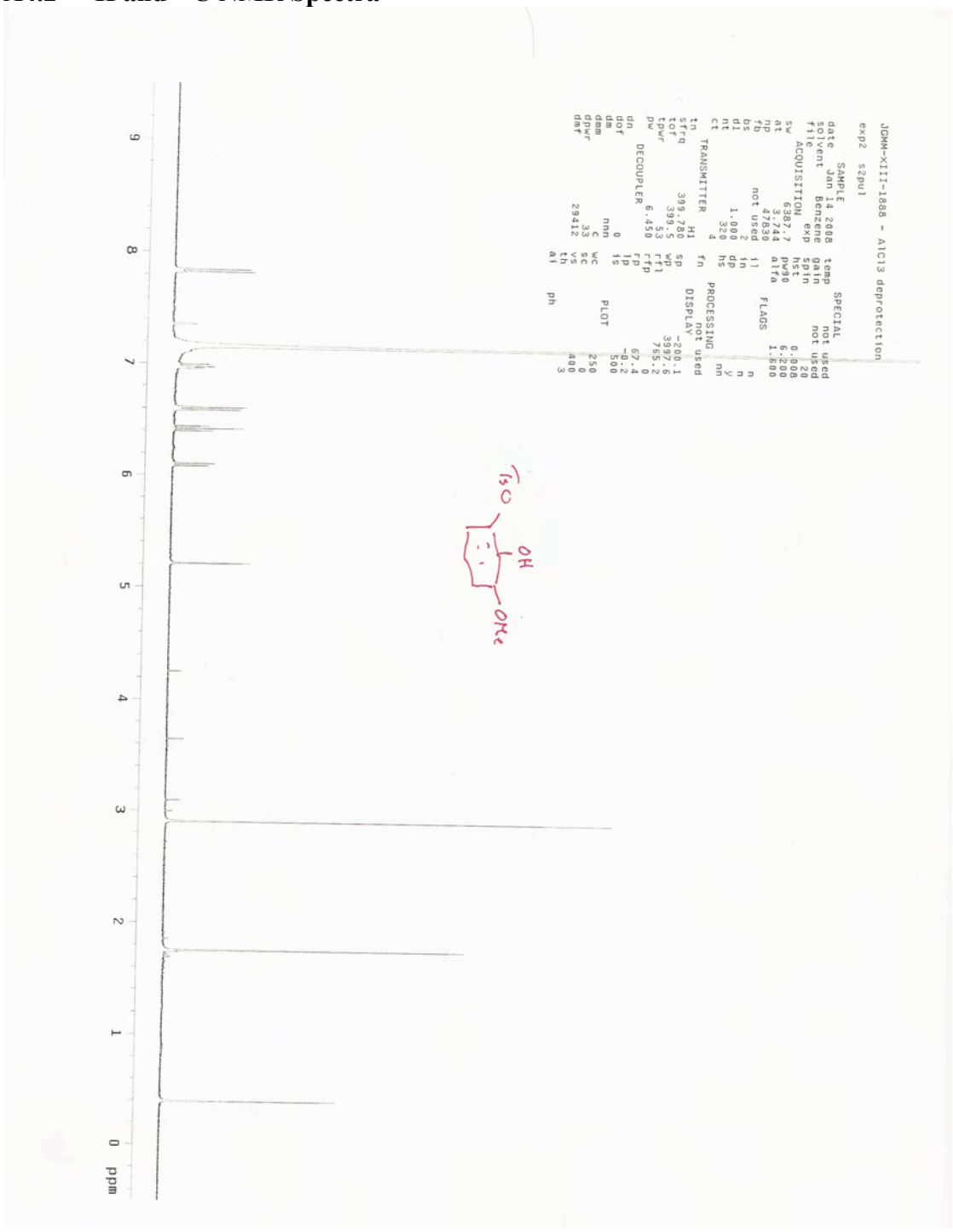
Vinyl Iodide Bicycle 4.39: In a flame-dried flask under N_2 atmosphere with magnetic stirring was combined acid **4.34** (500 mg, 1.71 mmol, 2 eq.) and diphenic acid (**4.18**) (207 m, 0.855 mmol, 1 eq.) in 8.6 ml anhydrous CH_2Cl_2 at 0 ºC. Lead tetraacetate (379 mg, 0.855 mmol, 1 eq.) was added and the reaction mixture became yellow, then green. After 30 min the solution was brought to ambient temperature and stirred an additional 30 min. The CH_2Cl_2 was removed *in vacuo* on an N_2-purged rotary evaporator. Toluene (8.6 ml) was added and the solvent again removed *in vacuo*, then this was repeated twice again in order to remove all residual acetic acid. To this solid was then added 8.6 ml anhydrous CH_2Cl_2 and it was brought to 0 ºC. Solid 3',5'-dimethoxy-4'-hydroxyacetophenone (**4.35**) (168 mg, 0.855 mmol, 1.0 eq.) was added and the reaction stirred 15 min, then brought to ambient temperature for 2 h. The reaction mixture was then filtered through Celite with additional CH_2Cl_2 to give a yellow solution. The solvent was removed *in vacuo* and column chromatography employed (SiO_2; 5% AcOH/10% EtOAc/ 85% hexanes; then 40% EtOAc/60% hexanes) to provide first recovered acid **4.34**, then the desired ketal (226 mg, 54% yield).

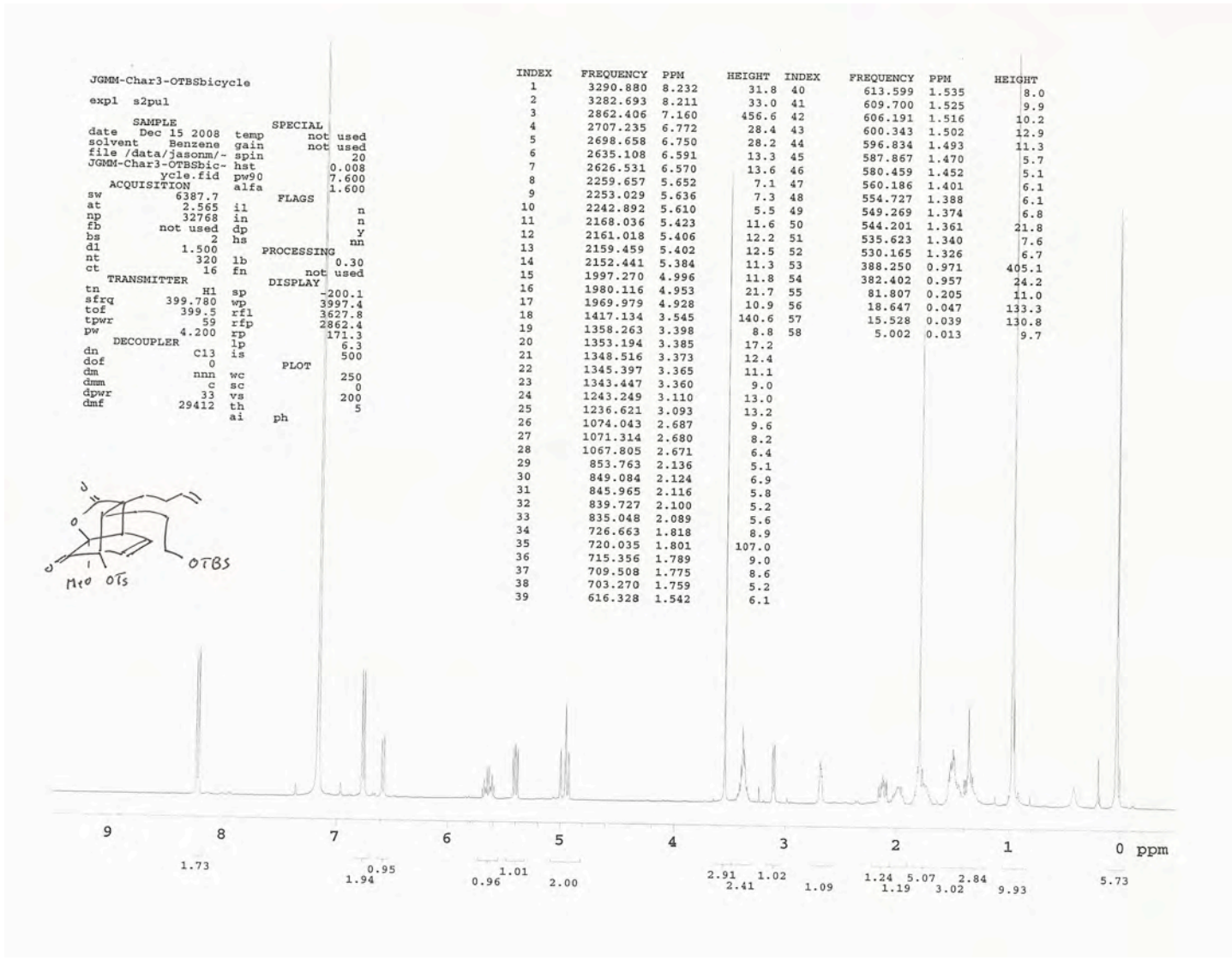
The oxidative dearomatization product above was taken up in 9.3 ml anhydrous PhMe under N_2 atmosphere with magnetic stirring and heated at 70 ºC for 15 h. Removal of the solvent *in vacuo* and column chromatography (SiO_2; 20% EtOAc/Hex) provided the bicycle **4.39** (119 mg, 53% yield) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 6.46 (dd, *J* = 1.1, 2.1, 1H), 5.88 (dddd, *J* = 5.6, 8.8, 10.0, 17.1, 1H), 5.61 (dd, *J* = 1.2, 2.9, 1H), 5.45 (d, *J* = 1.7, 1H), 5.27 – 5.14 (m, 2H), 4.51 (d, *J* = 2.2, 1H), 3.36 (s, 3H), 3.21 (s, 3H), 2.70 (ddt, *J* = 1.2, 5.7, 13.5, 1H), 2.48 (ddd, *J* = 0.9, 3.2, 8.5, 1H), 2.20 – 2.14 (m, 1H), 2.08 (dddd, *J* = 1.2, 6.5, 9.4, 14.6, 1H), 1.75 (dd, *J* = 8.8, 13.4, 1H), 1.77 – 1.69 (m, 1H), 1.58 (s, 3H), 1.21 – 1.12 (m, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ 195.5, 192.6, 174.4, 141.0, 138.8, 131.8, 127.0, 122.1, 110.5, 97.7, 87.7, 54.0, 53.4, 52.8, 46.1, 45.6, 41.8, 33.8, 24.7, 24.2; FTIR (thin film, KCl) 3078, 2966, 2899, 2830, 1767, 1677, 1612, 1443, 1380, 1241, 1163, 1051, 942, 883, 808, 690, 594, 520 cm^{-1}.



Stepwise Bicycle 4.40: In a flame-dried flask under N_2 atmosphere with magnetic stirring was dissolved vinyl iodide **4.39** (51 mg, 105 μmol, 1.0 eq.) in 2.1 ml anhydrous PhMe. The solution was brought to 80 ^{o}C, then *n*-Bu_3SnH (33 μl, 126 μmol, 1.2 eq.) and AIBN (1.7 mg, 10.5 μmol, 0.1 eq.) were added. The reaction mixture was refluxed for 2 h, then an additional 1.7 mg AIBN was added. After an additional 2 h stirring, the reaction mixture was brought to ambient temperature and the solvent was removed *in vacuo*. The crude oil was subjected to column chromatography (SiO_2; 20 → 30 → 40% EtOAc/Hex) to provide the cyclization product **4.40** (12.3 mg, 40% yield) as a white solid. ^{1}H NMR (400 MHz, C_6D_6) δ 6.23 (ddt, *J* = 7.1, 10.3, 17.2, 1H), 5.83 (d, *J* = 17.2, 1H), 5.33 (dd, *J* = 2.1, 10.3, 1H), 4.66 (s, 1H), 4.50 (s, 1H), 3.50 (s, 4H), 3.04 (d, *J* = 12.1, 1H), 2.96 (s, 1H), 2.94 (s, 3H), 2.83 (t, *J* = 6.3, 2H), 2.65 (d, *J* = 12.1, 1H), 2.30 (s, 1H), 1.99 – 1.84 (m, 1H), 1.77 – 1.62 (m, 1H), 1.50 (s, 3H) 1.37 – 1.22 (m, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ 205.4, 202.8, 175.7, 142.2, 133.1, 121.7, 115.8, 102.8, 82.8, 54.0, 52.1, 51.7, 48.4, 44.7, 41.7, 35.3, 33.4, 30.4, 27.6, 21.6; FTIR (thin film, KCl) 3078, 2950, 2850, 1788, 1758, 1712, 1445, 1316, 1240, 1184, 1114, 1082, 980, 908, 682, 556 cm^{-1}.

A4.2 ^{1}H and ^{13}C NMR Spectra

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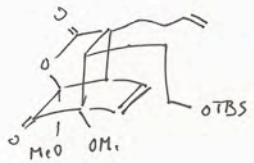
51 535.623 1.340 7.6
52 530.165 1.326 6.7
53 388.250 0.971 405.1
54 382.402 0.957 24.2
55 81.807 0.205 11.0
56 18.647 0.047 133.3
57 15.528 0.039 130.8
58 5.002 0.013 9.7
O
O
I
OTBS
MeO OTs
9
8
7
6
5
4
3
2
1
0 ppm
1.73
1.94
0.95
0.96
1.01
2.00
2.91
2.41
1.02
1.09
1.24
1.19
5.07
3.02
2.84
9.93
5.73

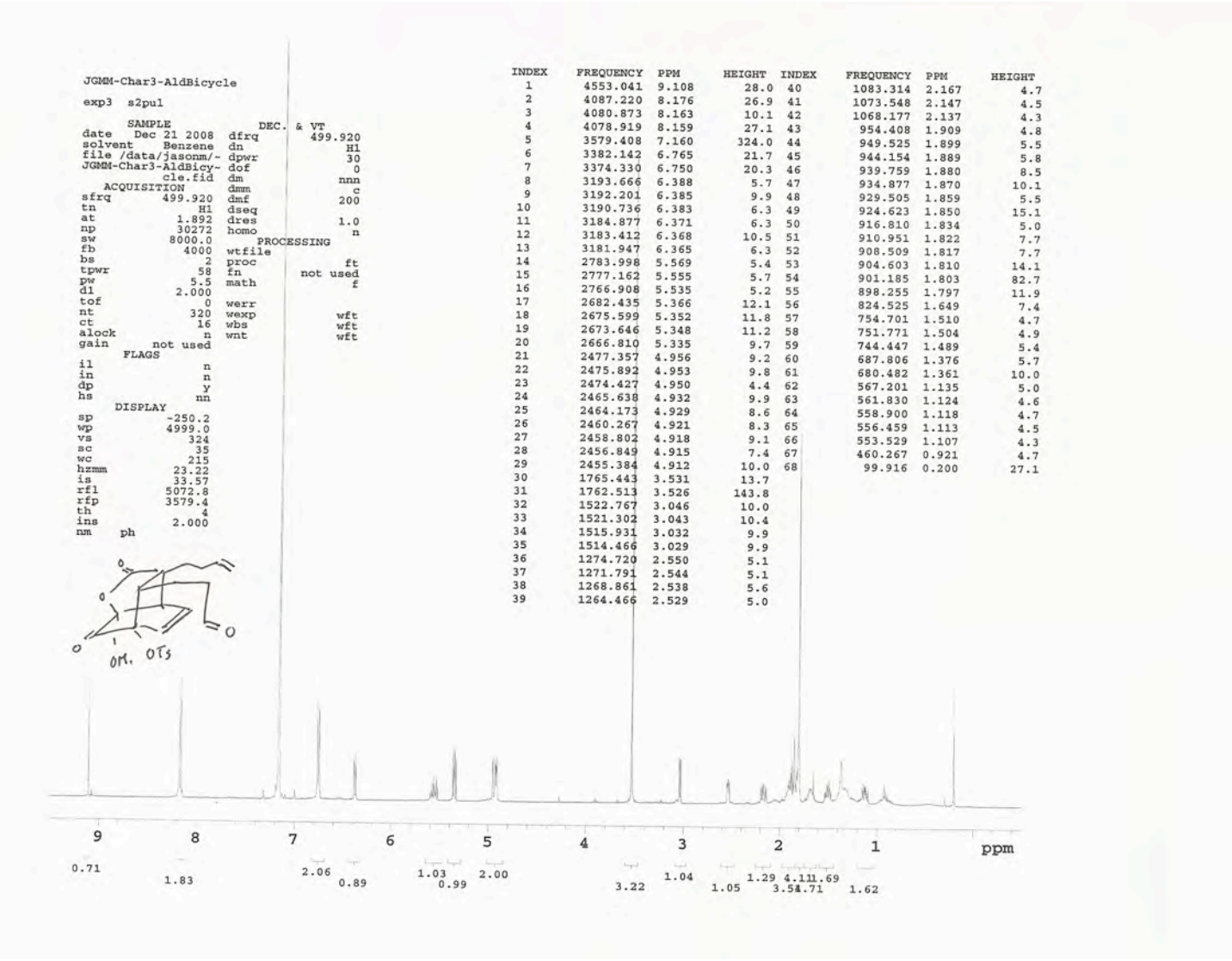
JGMM-Char3-OTBSbicycleC

exp3 s2pul

SAMPLE		DEC. & VT	
date	Dec 21 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/-	dpwr	40
JGMM-Char3-OTBSbic-		dof	0
	ycleC.fid	dm	yyy
ACQUISITION		dmm	w
sfrq	125.717	dmf	13333
tn	C13	dseq	
at	1.300	dres	1.0
np	75146	homo	n
sw	28891.3	PROCESSING	
fb	16000	lb	0.50
bs	4	wtfile	
tpwr	53	proc	ft
pw	6.0	fn	not used
dl	1.200	math	f
tof	1255.5		
nt	24000	werr	
ct	2648	wexp	wft
alock	n	wbs	wft
gain	not used	wnt	
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1237.3		
wp	28890.9		
vs	2084		
sc	0		
wc	250		
hzmm	115.56		
is	500.00		
rfl	17327.9		
rfp	16090.1		
th	8		
ins	100.000		
nm cdc ph			



INDEX	FREQUENCY	PPM	HEIGHT
1	24255.940	192.960	8.9
2	21921.218	174.387	12.1
3	18210.616	144.869	14.4
4	17274.259	137.420	35.7
5	17043.696	135.586	13.3
6	16559.206	131.731	32.1
7	16292.494	129.610	76.9
8	16191.540	128.807	72.7
9	16126.736	128.291	163.0
10	16114.392	128.193	1987.6
11	16102.930	128.102	75.4
12	16090.146	128.000	2061.5
13	16078.243	127.905	88.1
14	16065.899	127.807	2084.4
15	15884.711	126.366	31.5
16	14538.808	115.659	33.8
17	12156.034	96.703	17.7
18	11631.427	92.530	23.4
19	7892.170	62.784	38.8
20	6855.740	54.539	34.6
21	6763.163	53.802	25.3
22	6382.272	50.772	37.7
23	5791.097	46.069	33.1
24	4205.373	33.454	37.4
25	3791.419	30.161	9.3
26	3716.034	29.562	35.8
27	3541.459	28.173	32.4
28	3287.972	26.156	129.7
29	3274.747	26.051	8.0
30	2799.074	22.267	33.7
31	2654.476	21.117	34.9
32	2318.111	18.441	15.5
33	-659.806	-5.249	29.1
34	-664.655	-5.287	27.6



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	4553.041	9.108	28.0	40	1083.314	2.167	4.7
2	4087.220	8.176	26.9	41	1073.548	2.147	4.5
3	4080.873	8.163	10.1	42	1068.177	2.137	4.3
4	4078.919	8.159	27.1	43	954.408	1.909	4.8
5	3579.408	7.160	324.0	44	949.525	1.899	5.5
6	3382.142	6.765	21.7	45	944.154	1.889	5.8
7	3374.330	6.750	20.3	46	939.759	1.880	8.5
8	3193.666	6.388	5.7	47	934.877	1.870	10.1
9	3192.201	6.385	9.9	48	929.505	1.859	5.5
10	3190.736	6.383	6.3	49	924.623	1.850	15.1
11	3184.877	6.371	6.3	50	916.810	1.834	5.0
12	3183.412	6.368	10.5	51	910.951	1.822	7.7
13	3181.947	6.365	6.3	52	908.509	1.817	7.7
14	2783.998	5.569	5.4	53	904.603	1.810	14.1
15	2777.162	5.555	5.7	54	901.185	1.803	82.7
16	2766.908	5.535	5.2	55	898.255	1.797	11.9
17	2682.435	5.366	12.1	56	824.525	1.649	7.4
18	2675.599	5.352	11.8	57	754.701	1.510	4.7
19	2673.646	5.348	11.2	58	751.771	1.504	4.9
20	2666.810	5.335	9.7	59	744.447	1.489	5.4
21	2477.357	4.956	9.2	60	687.806	1.376	5.7
22	2475.892	4.953	9.8	61	680.482	1.361	10.0
23	2474.427	4.950	4.4	62	567.201	1.135	5.0
24	2465.638	4.932	9.9	63	561.830	1.124	4.6
25	2464.173	4.929	8.6	64	558.900	1.118	4.7
26	2460.267	4.921	8.3	65	556.459	1.113	4.5
27	2458.802	4.918	9.1	66	553.529	1.107	4.3
28	2456.849	4.915	7.4	67	460.267	0.921	4.7
29	2455.384	4.912	10.0	68	99.916	0.200	27.1
30	1765.443	3.531	13.7				
31	1762.513	3.526	143.8				
32	1522.767	3.046	10.0				
33	1521.302	3.043	10.4				
34	1515.931	3.032	9.9				
35	1514.466	3.029	9.9				
36	1274.720	2.550	5.1				
37	1271.791	2.544	5.1				
38	1268.861	2.538	5.6				
39	1264.466	2.529	5.0				

JGMM-Char3-AldBicycleC

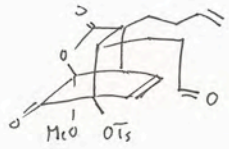
exp3 s2pul

SAMPLE		DEC. & VT	
date	Dec 21 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	40
	JGMM-Char3-AldBicy~	dof	0
	cleC.fid	dm	YYY
ACQUISITION		dmm	w
sfrq	125.717	dmf	13333
tn	C13	dseq	
at	1.300	dres	1.0
np	97690	homo	n
sw	37558.7	PROCESSING	
fb	21000	lb	0.50
bs	4	wtfile	
tpwr	53	proc	ft
pw	6.0	fn	not used
d1	1.200	math	f
tof	1255.5		
nt	25000	werr	
ct	1144	wexp	wft
alock	n	wbs	wft
gain	not used	wnt	

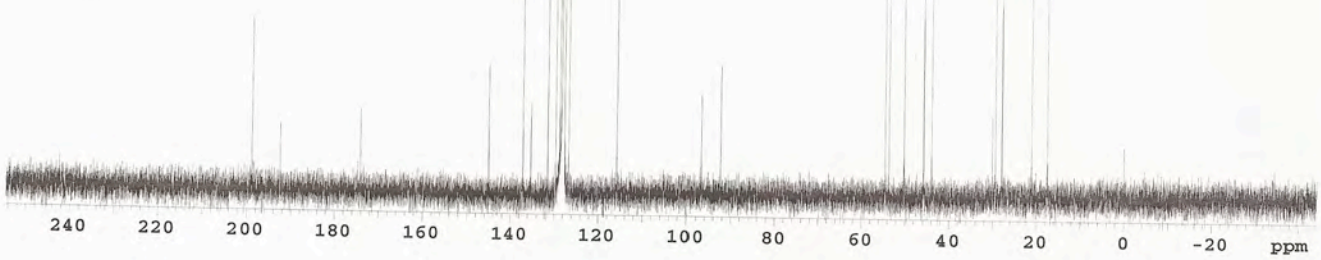
FLAGS	
il	n
in	n
dp	y
hs	nn

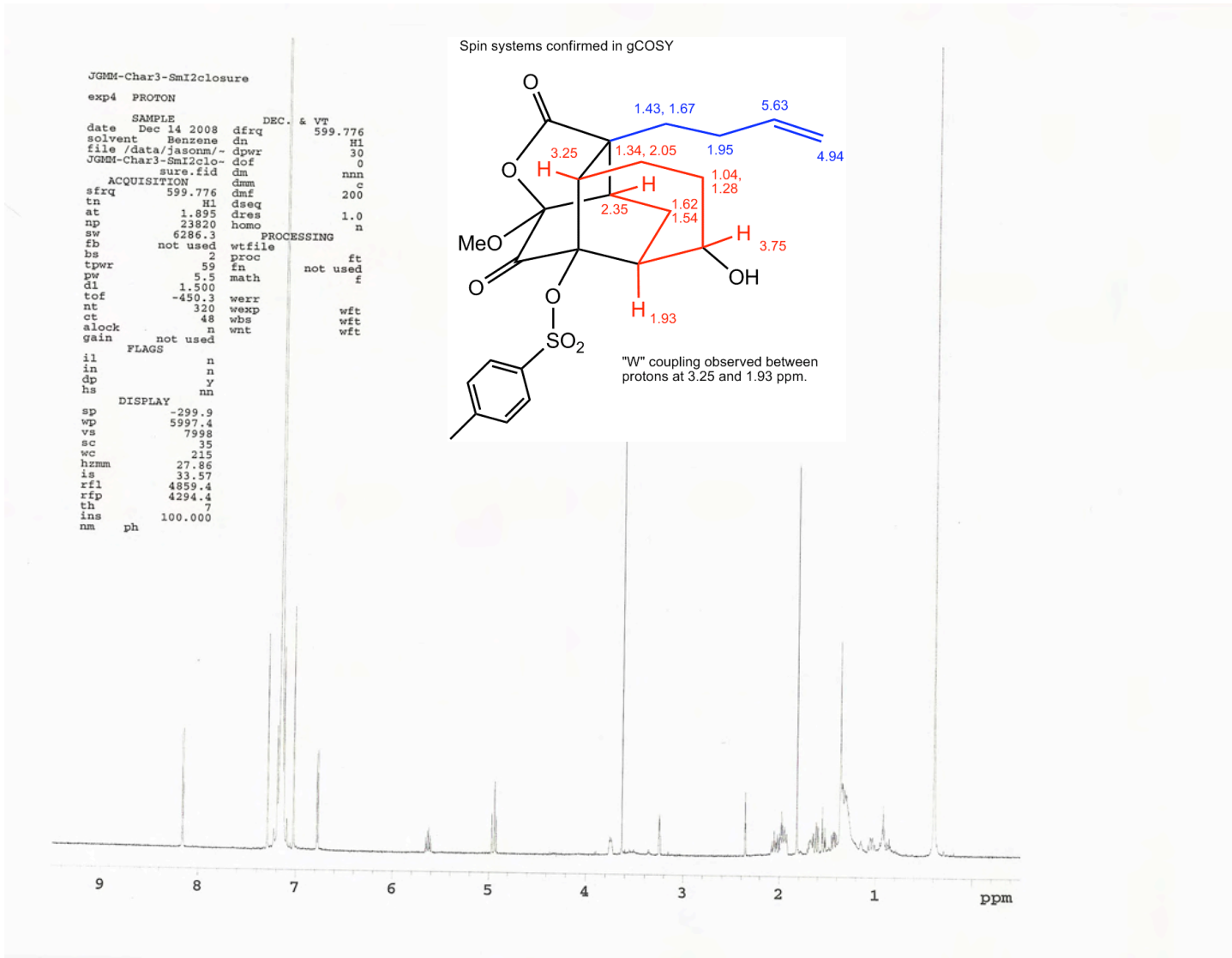
DISPLAY	
sp	-5570.7
wp	37558.1
vs	3027
sc	0
wc	250
hzmm	150.23
is	500.00
rfl	21661.5
rfp	16090.1
th	11
ins	100.000

nm cdc ph



INDEX	FREQUENCY	PPM	HEIGHT
1	25008.156	198.944	31.9
2	24201.231	192.525	11.5
3	21896.796	174.193	14.5
4	18235.832	145.069	23.7
5	17243.223	137.173	41.0
6	17013.410	135.345	16.0
7	16529.140	131.492	43.7
8	16302.766	129.691	111.9
9	16184.134	128.748	120.3
10	16126.824	128.292	197.1
11	16114.216	128.191	2893.9
12	16103.900	128.109	89.2
13	16090.146	128.000	3016.2
14	16078.684	127.909	103.9
15	16066.076	127.809	3027.3
16	15930.251	126.728	46.4
17	14555.957	115.795	49.6
18	12164.983	96.775	18.3
19	11613.661	92.389	23.8
20	6860.942	54.580	49.5
21	6747.469	53.677	37.6
22	6311.339	50.208	49.8
23	5762.310	45.840	41.7
24	5525.619	43.957	60.0
25	3791.992	30.166	14.4
26	3703.161	29.459	49.1
27	3509.453	27.918	41.5
28	2654.961	21.121	47.2
29	2200.493	17.505	46.6



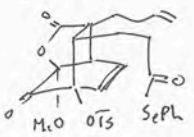

JGMM-Char3-SmI2closure
exp4 PROTON
SAMPLE
date Dec 14 2008
solvent Benzene
file /data/jasonm/~
JGMM-Char3-SmI2clo~
sure.fid
ACQUISITION
sfrq 599.776
tn H1
at 1.895
np 23820
sw 6286.3
fb not used
bs 2
tpwr 59
pw 5.5
d1 1.500
tof -450.3
nt 320
ct 48
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -299.9
wp 5997.4
vs 7998
sc 35
wc 215
hzmm 27.86
is 33.57
rfl 4859.4
rfp 4294.4
th 7
ins 100.000
nm ph
DEC. & VT
dfrq 599.776
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp wft
wbs wft
wnt wft
Spin systems confirmed in gCOSY
1.43, 1.67
5.63
3.25
1.34, 2.05
1.95
4.94
1.04,
1.28
2.35
1.62
1.54
3.75
MeO
OH
1.93
"W" coupling observed between protons at 3.25 and 1.93 ppm.
9
8
7
6
5
4
3
2
1
ppm

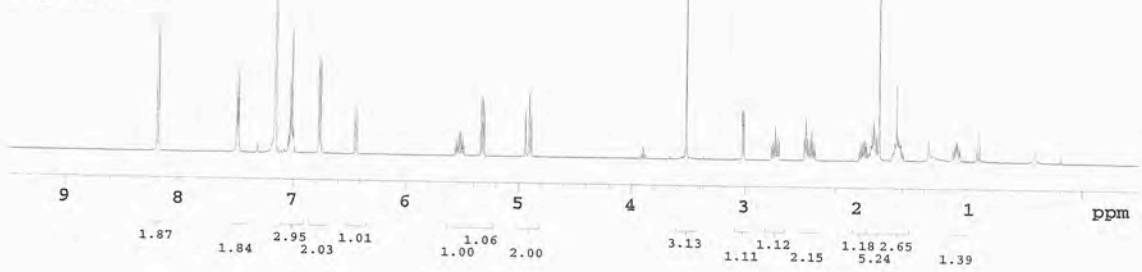
JGMM-Char3-SePhBicycle

exp3 s2pul

SAMPLE		DEC. & VT	
date	Dec 28 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
	JGMM-Char3-SePhBic~	dof	0
	ycle.fid	dm	nnn
ACQUISITION		dmm	c
sfrq	499.920	dmf	200
tn	H1	dseq	
at	1.892	dres	1.0
np	30272	homo	n
sw	8000.0	temp	21.0
fb	4000	PROCESSING	
bs	4	wtfile	
tpwr	58	proc	ft
pw	5.5	fn	not used
dl	2.000	math	f
tof	0		
nt	320	werr	
ct	8	wexp	wft
alock	n	wbs	wft
gain	not used	wnt	wft
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	55		
sc	35		
wc	215		
hzmm	23.22		
is	33.57		
rfl	5073.2		
rfp	3579.4		
th	3		
ins	2.000		
ai	ph		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM
1	4098.451	8.198	3.4	40	2443.177	4.887	7.0	79	566.224	1.133
2	4096.498	8.194	23.8	41	1759.584	3.520	143.5	80	561.341	1.123
3	4094.544	8.190	8.3	42	1513.002	3.027	9.2	81	557.923	1.116
4	4089.662	8.181	7.6	43	1511.537	3.024	9.6	82	555.970	1.112
5	4088.197	8.178	23.8	44	1506.166	3.013	9.1	83	552.552	1.105
6	3749.330	7.500	15.3	45	1504.701	3.010	9.3	84	460.267	0.921
7	3746.888	7.495	11.0	46	1377.259	2.755	3.4	85	452.943	0.906
8	3745.423	7.492	5.7	47	1372.377	2.745	3.5			
9	3742.982	7.487	7.9	48	1366.517	2.733	6.7			
10	3741.517	7.484	15.5	49	1360.658	2.722	3.8			
11	3739.564	7.480	14.3	50	1355.775	2.712	4.3			
12	3579.408	7.160	244.2	51	1349.916	2.700	3.6			
13	3518.373	7.038	5.4	52	1239.076	2.479	4.2			
14	3516.908	7.035	3.5	53	1233.705	2.468	8.2			
15	3513.002	7.027	14.5	54	1228.334	2.457	4.5			
16	3508.607	7.018	10.5	55	1222.962	2.446	3.7			
17	3505.677	7.013	23.8	56	1218.080	2.437	4.1			
18	3501.283	7.004	5.5	57	1211.732	2.424	4.1			
19	3499.818	7.001	4.6	58	1206.849	2.414	5.9			
20	3386.537	6.774	18.7	59	1201.478	2.403	3.5			
21	3378.236	6.758	18.4	60	982.240	1.965	3.6			
22	3227.357	6.456	5.4	61	976.869	1.954	3.5			
23	3225.892	6.453	9.3	62	972.474	1.945	4.1			
24	3224.427	6.450	5.6	63	967.103	1.935	4.2			
25	3218.568	6.438	5.5	64	961.732	1.924	3.6			
26	3217.103	6.435	9.1	65	935.853	1.872	6.2			
27	2765.931	5.533	4.5	66	929.017	1.858	7.9			
28	2759.095	5.519	4.9	67	925.599	1.852	6.4			
29	2748.841	5.499	4.1	68	921.693	1.844	3.5			
30	2668.763	5.338	11.1	69	915.834	1.832	5.1			
31	2661.927	5.325	11.2	70	910.951	1.822	3.7			
32	2659.974	5.321	11.0	71	903.138	1.807	74.1			
33	2653.138	5.307	10.2	72	830.384	1.661	3.7			
34	2471.009	4.943	7.1	73	824.037	1.648	14.9			
35	2469.544	4.940	8.7	74	818.666	1.638	5.2			
36	2468.080	4.937	3.7	75	814.759	1.630	4.1			
37	2453.919	4.909	12.9	76	812.806	1.626	4.1			
38	2452.455	4.906	11.2	77	804.017	1.608	3.5			
39	2444.642	4.890	7.9	78	680.482	1.361	4.5			



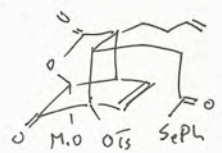


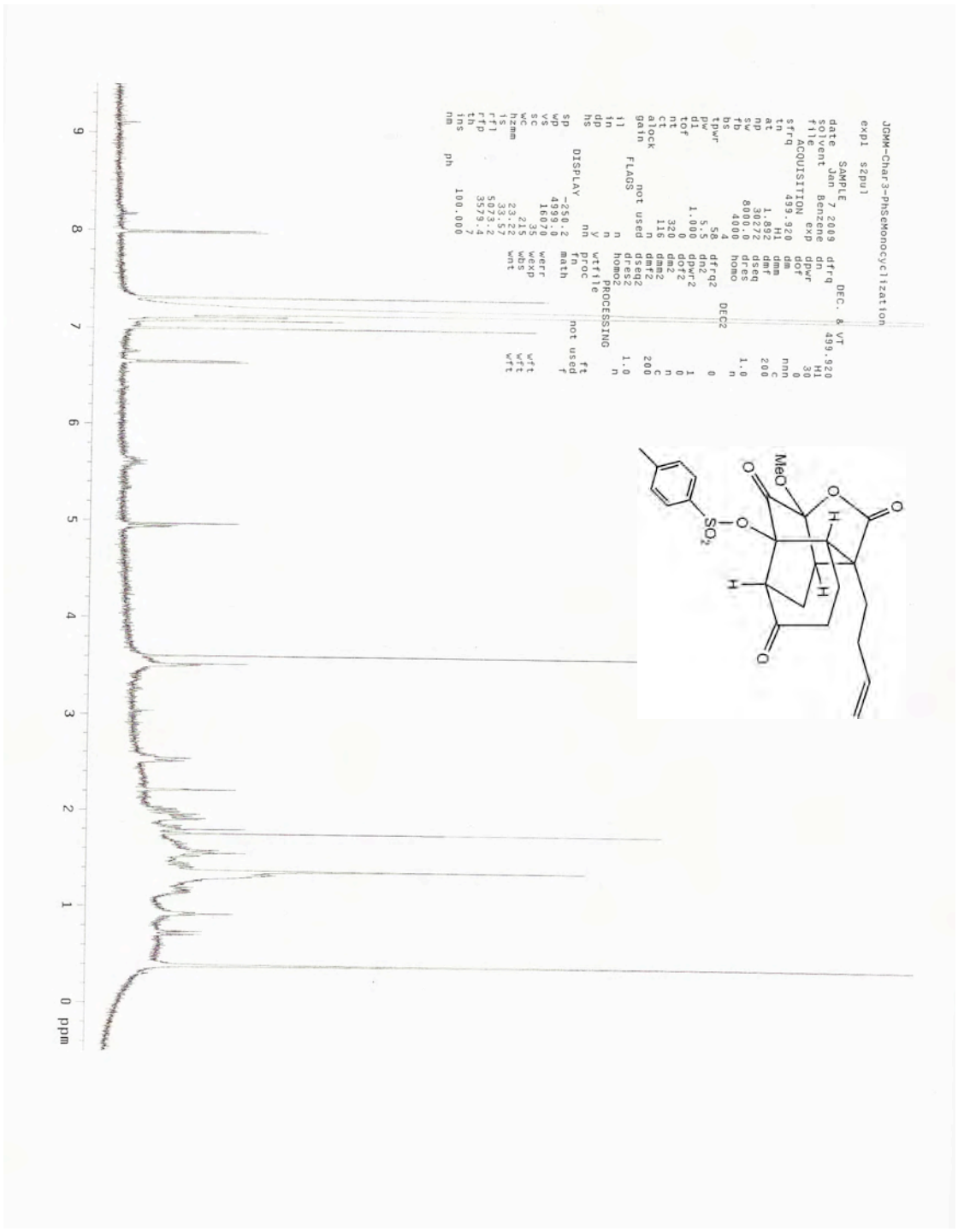
JGMM-Char3-SePhBicycleC

exp3 s2pul

SAMPLE		DEC. & VT	
date	Dec 28 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jascnm/~	dpwr	40
JGMM-Char3-SePhBic~		dof	0
	ycleC.fid	dm	yyy
ACQUISITION		dmm	w
sfrq	125.717	dmf	13333
tn	C13	dseq	
at	1.300	dres	1.0
np	75146	homo	n
sw	28891.3	temp	21.0
fb	16000	PROCESSING	
bs	4	lb	0.50
tpwr	53	wtfile	
pw	6.0	proc	ft
dl	1.500	fn	not used
tof	1255.5	math	f
nt	32000		
ct	1000	werr	
alock	n	wexp	wft
gain	not used	wbs	wft
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1246.3		
wp	28890.9		
vs	1503		
sc	0		
wc	250		
hzmm	115.56		
is	500.00		
rfl	1246.7		
rfp	0		
th	9		
ins	100.000		
nm cdc ph			

INDEX	FREQUENCY	PPM	HEIGHT
1	24853.128	197.711	11.1
2	24172.020	192.293	11.8
3	21854.933	173.860	12.3
4	18235.585	145.067	16.5
5	17226.929	137.043	28.2
6	17097.320	136.012	56.3
7	16992.840	135.181	11.5
8	16490.716	131.187	20.9
9	16302.916	129.693	55.0
10	16268.530	129.419	50.9
11	16196.672	128.847	29.6
12	16179.479	128.711	51.6
13	16118.201	128.223	102.7
14	16105.857	128.125	1441.8
15	16093.954	128.030	45.7
16	16081.611	127.932	1489.4
17	16070.149	127.841	54.9
18	16057.364	127.739	1502.9
19	15941.862	126.820	10.9
20	15932.164	126.743	20.8
21	14544.821	115.707	27.6
22	12143.532	96.604	18.8
23	11562.937	91.985	17.6
24	6852.936	54.516	25.8
25	6718.919	53.450	22.9
26	6207.978	49.386	23.6
27	5936.858	47.229	25.0
28	5753.466	45.770	22.1
29	3690.306	29.357	25.5
30	3510.441	27.926	20.8
31	2649.909	21.080	27.9
32	2641.533	21.014	20.6




JOMM-Char3-PhSemonocyclization
expl szpul
SAMPLE
date Jan 7 2009
solvent Benzene
file exp
ACQUISITION
sfrq 499.920
tn H1
at 1.892
np 30272
sw 8000.0
fb 4000
bs 4
tpwr 50
pw 5.5
d1 1.000
tof 0
nt 320
ct 116
alock n
gain n
FLAGS
not used
n
n
y
nn
DISPLAY
-250.2
4499.0
1687.0
35
215
23.22
33.57
5073.2
3579.4
100.000
ph
dfrq DEC. & VT
dn 499.920
dpwr H1
dof 30
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmf2 c
dseq2 200
dres2
homo2 1.0
PROCESSING n
wtfile
proc
fn
not used
math
werr ft
wexp
wbs wft
wnt wft
wft
MeO
O
H
O
O
SO2
O
H
H
O
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1
0 ppm

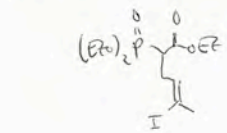
LK-III-40 - B-to-F vinyl iodide phosphonate

exp2 s2pul

SAMPLE		SPECIAL	
date	Nov 19 2008	temp	not used
solvent	Benzene	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	4789.3	pw90	14.000
at	3.000	alfa	-6.900
np	28736	FLAGS	
fb	not used	il	n
bs	2	in	n
ss	2	dp	y
dl	1.000	hs	nn
nt	4	PROCESSING	
ct	4	lb	0.30
TRANSMITTER		fn	65536
tn	H1	DISPLAY	
sfrq	299.763	sp	-149.9
tof	265.1	wp	2997.5
tpwr	58	rfl	2728.8
pw	5.600	rfp	2146.3
DECOUPLER		rp	124.8
dn	C13	lp	-1.6
dof	0	PLOT	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	46	vs	368
dmf	13100	th	4
		ai ph	

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY
1	2146.290	7.160	54.7	40	946.597	3.158	6.9	79	311.672
2	1627.709	5.430	10.5	41	941.920	3.142	10.5	80	310.941
3	1621.132	5.408	21.2	42	940.897	3.139	10.8	81	304.510
4	1614.701	5.387	11.6	43	937.389	3.127	12.7	82	303.779
5	1228.689	4.099	5.2	44	936.366	3.124	12.5	83	296.909
6	1227.665	4.095	4.9	45	924.234	3.083	4.3	84	295.886
7	1225.619	4.089	5.4	46	914.149	3.050	5.5	85	289.747
8	1224.596	4.085	5.4	47	913.126	3.046	4.9	86	288.724
9	1220.650	4.072	14.1	48	909.764	3.035	7.6	87	282.732
10	1218.457	4.065	20.6	49	908.741	3.032	8.2	88	281.562
11	1217.434	4.061	21.8	50	907.718	3.028	7.6		
12	1213.488	4.048	23.7	51	903.333	3.014	8.0		
13	1211.441	4.041	37.1	52	902.164	3.010	7.3		
14	1210.272	4.037	40.3	53	899.533	3.001	10.2		
15	1205.449	4.021	31.7	54	892.956	2.979	9.1		
16	1204.426	4.018	38.6	55	891.933	2.975	7.7		
17	1203.256	4.014	49.5	56	889.302	2.967	5.5		
18	1198.579	3.998	23.3	57	882.724	2.945	4.3		
19	1196.095	3.990	57.3	58	872.055	2.909	5.0		
20	1195.364	3.988	65.1	59	870.885	2.905	4.4		
21	1191.710	3.976	16.0	60	866.500	2.891	7.0		
22	1188.202	3.964	72.0	61	865.477	2.887	8.9		
23	1181.040	3.940	42.4	62	864.162	2.883	5.9		
24	1179.871	3.936	34.0	63	860.946	2.872	8.9		
25	1178.263	3.931	14.8	64	856.269	2.857	9.2		
26	1173.878	3.916	10.7	65	854.808	2.852	9.0		
27	1172.855	3.913	10.6	66	853.346	2.847	7.8		
28	1171.101	3.907	5.0	67	851.007	2.839	7.7		
29	974.075	3.250	6.8	68	849.984	2.836	7.7		
30	973.198	3.247	7.0	69	846.622	2.824	5.9		
31	969.398	3.234	8.1	70	639.512	2.133	147.4		
32	968.375	3.230	8.1	71	329.649	1.100	49.4		
33	963.990	3.216	9.8	72	328.919	1.097	50.9		
34	962.967	3.212	9.9	73	322.634	1.076	98.5		
35	959.167	3.200	10.6	74	321.903	1.074	101.4		
36	958.290	3.197	10.5	75	318.687	1.063	63.9		
37	952.005	3.176	6.1	76	317.957	1.061	62.8		
38	951.128	3.173	6.3	77	315.618	1.053	58.6		
39	947.620	3.161	6.9	78	314.887	1.050	58.0		

Char



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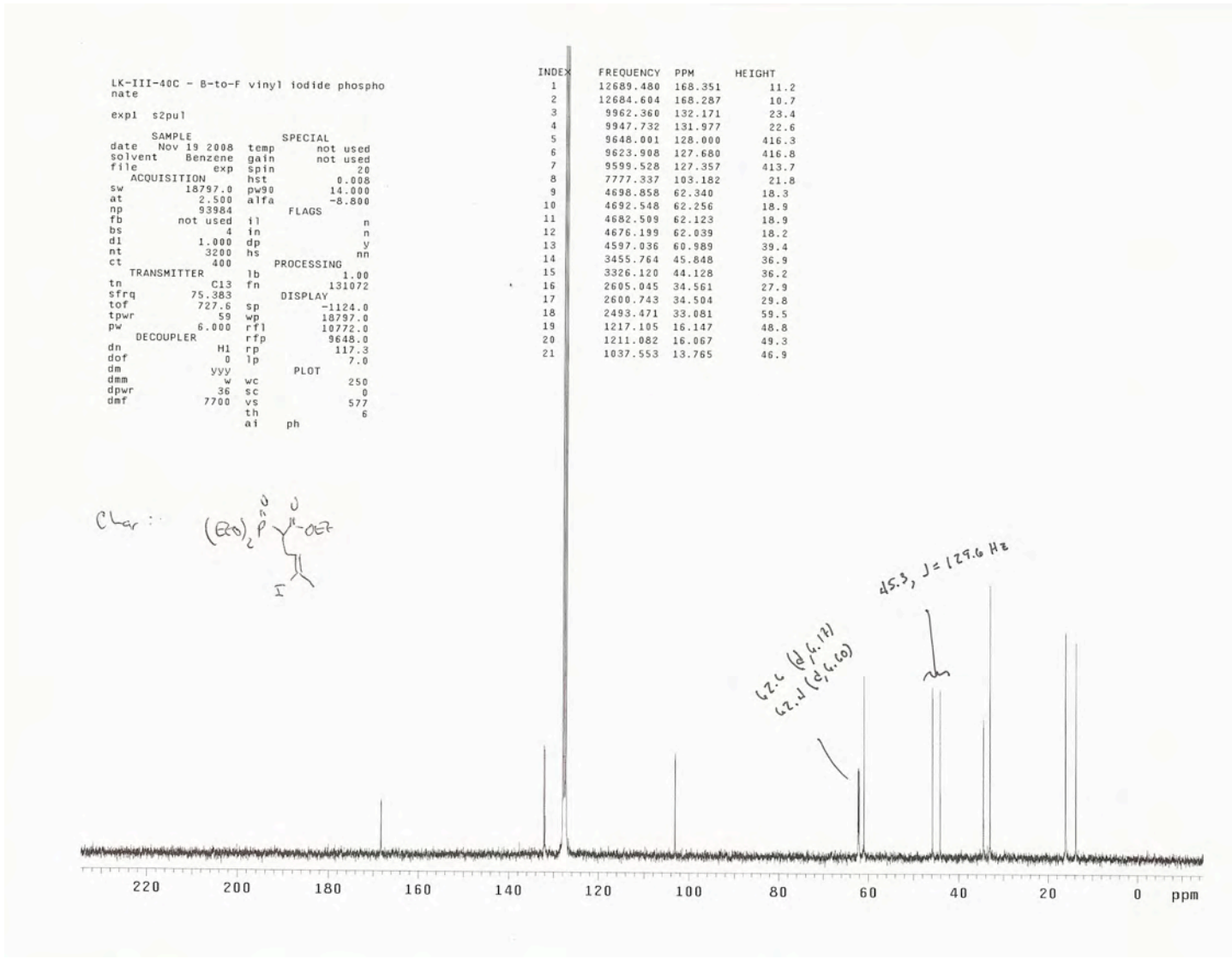
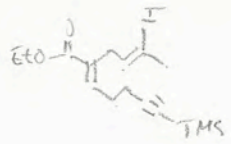

LK-III-40C - B-to-F vinyl iodide phospho
nate
expl s2pul
SAMPLE
date Nov 19 2008
solvent Benzene
file exp
ACQUISITION
sw 18797.0
at 2.500
np 93984
fb not used
bs 4
dl 1.000
nt 3200
ct 400
TRANSMITTER
tn C13
sfrq 75.383
tof 727.6
tpwr 59
pw 6.000
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 36
dmf 7700
SPECIAL
temp not used
gain not used
spin 20
hst 0.008
pw90 14.000
alfa -8.800
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn 131072
DISPLAY
sp -1124.0
wp 18797.0
rfl 10772.0
rfp 9648.0
rp 117.3
lp 7.0
PLOT
wc 250
sc 0
vs 577
th 6
ai ph
INDEX FREQUENCY PPM HEIGHT
1 12689.480 168.351 11.2
2 12684.604 168.287 10.7
3 9962.360 132.171 23.4
4 9947.732 131.977 22.6
5 9648.001 128.000 416.3
6 9623.908 127.680 416.8
7 9599.528 127.357 413.7
8 7777.337 103.182 21.8
9 4698.858 62.340 18.3
10 4692.548 62.256 18.9
11 4682.509 62.123 18.9
12 4676.199 62.039 18.2
13 4597.036 60.989 39.4
14 3455.764 45.848 36.9
15 3326.120 44.128 36.2
16 2605.045 34.561 27.9
17 2600.743 34.504 29.8
18 2493.471 33.081 59.5
19 1217.105 16.147 48.8
20 1211.082 16.067 49.3
21 1037.553 13.765 46.9
CLar :
45.3, J = 129.6 Hz
62.6 (d, 4.1)
62.1 (d, 4.6)
220
200
180
160
140
120
100
80
60
40
20
0
ppm

LK-III-42 - HWE, B-to-F vinyl iodide

exp3 s2pul

SAMPLE		SPECIAL	
date	Nov 24 2008	temp	not used
solvent	Benzene	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	4789.3	pw90	14.000
at	3.000	alfa	-6.900
np	28736	**FLAGS**	
fb	not used	il	n
bs	2	in	n
ss	2	dp	y
d1	1.000	hs	nn
nt	320	**PROCESSING**	
ct	4	lb	0.30
TRANSMITTER		fn	65536
tn	H1	**DISPLAY**	
sfrq	299.763	sp	-149.9
tof	265.1	wp	2997.5
tpwr	58	rfl	2729.1
pw	5.600	rfp	2146.3
DECOUPLER		rp	126.3
dn	C13	lp	-6.3
dof	0	**PLOT**	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	46	vs	222
dmf	13100	th	8
		ai	ph

INDEX	FREQUENCY	PPM	HEIGHT
1	2146.290	7.160	10.8
2	2077.156	6.929	14.2
3	2069.701	6.905	29.7
4	2062.247	6.880	14.5
5	1606.808	5.360	8.6
6	1605.347	5.355	9.2
7	1600.377	5.339	19.0
8	1598.915	5.334	19.6
9	1597.600	5.330	8.7
10	1593.946	5.317	9.5
11	1592.484	5.313	9.3
12	1211.588	4.042	22.4
13	1204.572	4.018	71.4
14	1197.410	3.995	73.1
15	1190.248	3.971	24.0
16	950.397	3.171	33.0
17	944.112	3.150	32.6
18	679.121	2.266	10.5
19	671.813	2.241	36.0
20	664.651	2.217	40.4
21	657.636	2.194	20.0
22	652.228	2.176	115.9
23	650.766	2.171	119.3
24	620.511	2.070	37.3
25	613.933	2.048	56.6
26	606.333	2.023	20.1
27	308.018	1.028	73.8
28	300.856	1.004	149.6
29	293.840	0.980	71.4
30	49.896	0.166	34.0
31	46.389	0.155	810.7
32	43.027	0.144	38.3

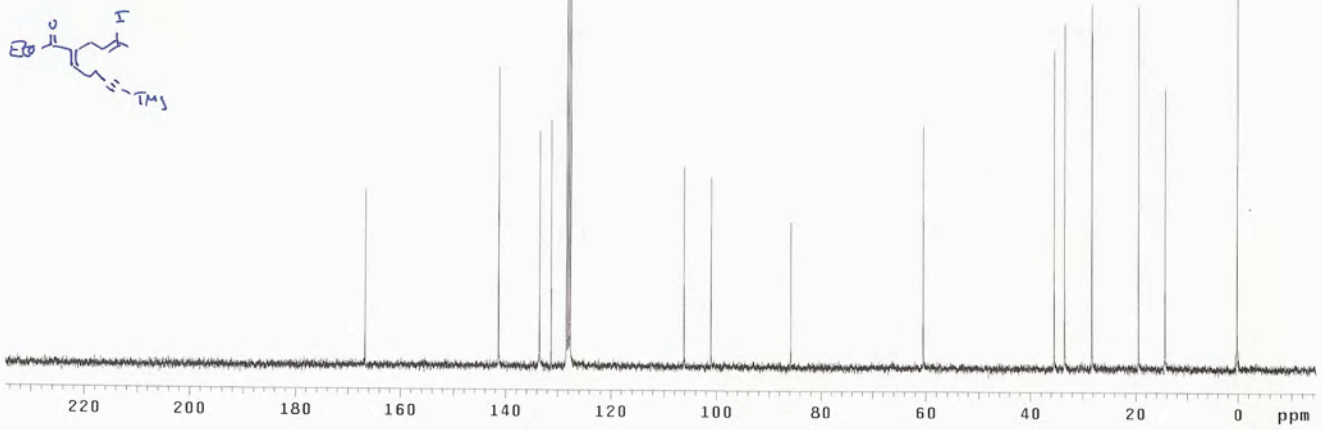


LK-III-42C - HWE, B-to-F vinyl iodide

expl s2pul

SAMPLE		SPECIAL	
date	Nov 24 2008	temp	not used
solvent	Benzene	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	18797.0	pw90	14.000
at	2.500	alfa	-8.800
np	93984	FLAGS	
fb	not used	il	n
bs	4	in	n
di	1.000	dp	y
nt	3200	hs	nn
ct	48	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	131072
sfrq	75.383	DISPLAY	
tof	727.6	sp	-1098.7
tpwr	59	wp	18797.0
pw	6.000	rfl	10746.7
DECOUPLER		rfp	9648.0
dn	H1	rp	115.3
dof	0	lp	13.5
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	36	sc	0
dmf	7700	vs	148
		th	17
		ai	ph

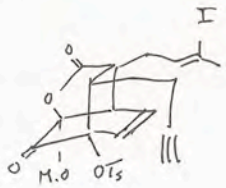
INDEX	FREQUENCY	PPM	HEIGHT
1	12566.143	166.715	33.2
2	10655.897	141.372	56.7
3	10062.458	133.499	44.6
4	9896.388	131.295	46.7
5	9672.091	128.320	118.3
6	9647.998	128.000	119.3
7	9623.618	127.677	118.9
8	8004.211	106.192	37.9
9	7617.860	101.066	35.8
10	6463.968	85.757	27.3
11	4561.466	60.517	45.8
12	2671.011	35.436	60.3
13	2520.716	33.442	65.5
14	2130.635	28.267	69.2
15	1467.212	19.466	69.0
16	1081.434	14.347	53.1
17	17.892	0.237	152.5



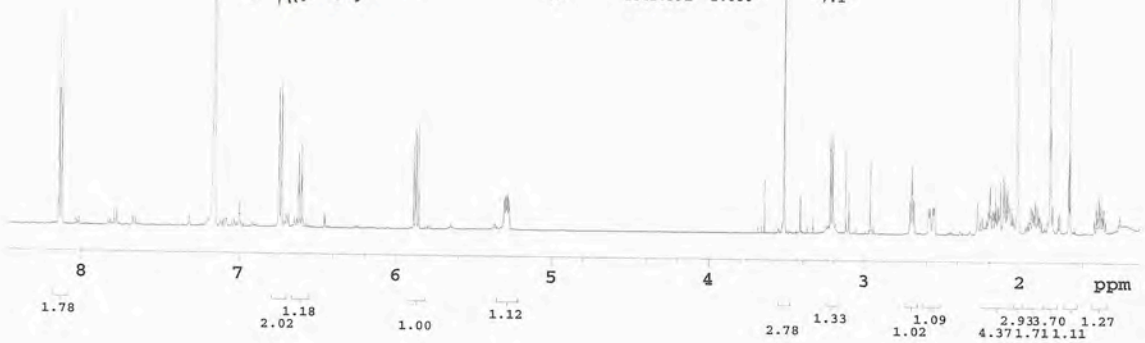
JGMM-Char3-BFvinylI

exp3 s2pul

SAMPLE		DEC. & VT	
date	Jan 3 2009	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
	JGMM-Char3-BFvinyl~	dof	0
	I.fid	dm	nnn
ACQUISITION		dmm	c
sfrq	499.920	dmf	200
tn	H1	dseq	
at	1.892	dres	1.0
np	30272	homo	n
sw	8000.0	PROCESSING	
fb	4000	wtfile	
bs	4	proc	ft
tpwr	58	fn	not used
pw	5.5	math	f
dl	2.000		
tof	0	werr	
nt	320	wexp	wft
ct	12	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	616.0		
wp	3612.3		
vs	378		
sc	35		
wc	215		
hzmm	16.78		
is	33.57		
rfl	5072.8		
rfp	3579.4		
th	5		
ins	1.000		
nm	ph		



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	4073.060	8.147	39.8	40	1341.127	2.683	6.7
2	4071.107	8.144	12.1	41	1280.091	2.561	5.5
3	4066.712	8.135	10.7	42	1278.138	2.557	5.7
4	4064.759	8.131	40.4	43	1275.209	2.551	5.6
5	3579.408	7.160	378.3	44	1137.025	2.274	6.2
6	3374.818	6.751	26.8	45	1135.560	2.271	6.6
7	3366.517	6.734	28.2	46	1097.474	2.195	8.5
8	3311.830	6.625	8.2	47	1095.521	2.191	9.6
9	3310.365	6.622	14.4	48	1078.431	2.157	9.5
10	3308.900	6.619	9.5	49	1075.990	2.152	5.6
11	3303.041	6.607	9.4	50	1072.084	2.145	5.7
12	3301.576	6.604	16.1	51	1069.642	2.140	5.7
13	3300.111	6.601	10.4	52	1063.294	2.127	10.6
14	2943.666	5.888	15.9	53	1054.017	2.108	11.2
15	2936.830	5.875	19.5	54	1049.623	2.100	10.6
16	2934.877	5.871	18.0	55	1046.693	2.094	5.6
17	2928.041	5.857	20.0	56	1044.252	2.089	9.0
18	2652.162	5.305	5.8	57	1039.857	2.080	10.1
19	2650.697	5.302	6.2	58	1037.904	2.076	6.2
20	2647.279	5.295	6.6	59	1034.974	2.070	6.8
21	2645.814	5.293	6.6	60	1033.509	2.067	5.6
22	2642.884	5.287	6.9	61	1010.072	2.020	45.7
23	2641.419	5.284	6.7	62	1008.607	2.018	78.5
24	2638.002	5.277	5.9	63	1007.142	2.015	45.3
25	1822.572	3.646	10.4	64	966.615	1.934	5.7
26	1760.072	3.521	277.8	65	961.732	1.924	5.6
27	1707.337	3.415	7.5	66	951.966	1.904	7.0
28	1610.658	3.222	16.7	67	945.619	1.892	5.9
29	1609.193	3.219	18.4	68	904.603	1.810	115.2
30	1603.822	3.208	15.7	69	901.673	1.804	20.7
31	1602.357	3.205	18.7	70	895.814	1.792	5.8
32	1560.853	3.122	16.3	71	845.521	1.691	14.2
33	1551.087	3.103	8.2	72	842.591	1.685	35.9
34	1481.752	2.964	14.2	73	840.150	1.681	16.4
35	1353.822	2.708	6.3	74	756.654	1.514	6.4
36	1352.357	2.705	6.5	75	747.865	1.496	7.6
37	1348.939	2.698	8.0	76	742.005	1.484	7.3
38	1347.474	2.695	13.3				
39	1342.591	2.686	7.1				



JGMM-Char3-BFvinylIC

expl s2pul

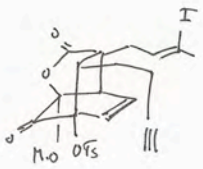
SAMPLE		DEC. & VT	
date	Jan 3 2009	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	40
JGMM-Char3-BFvinyl~		dof	0
	IC.fid	dm	YYY
ACQUISITION		dmm	w
sfrq	125.717	dmf	13333
tn	C13	dseq	
at	1.300	dres	1.0
np	75146	homo	n
sw	28891.3	PROCESSING	
fb	16000	lb	0.50
bs	4	wtfile	
tpwr	53	proc	ft
pw	6.0	fn	not used
dl	1.500	math	f
tof	1255.5		
nt	32000	werr	
ct	1124	wexp	wft
alock	n	wbs	wft
gain	not used	wnt	

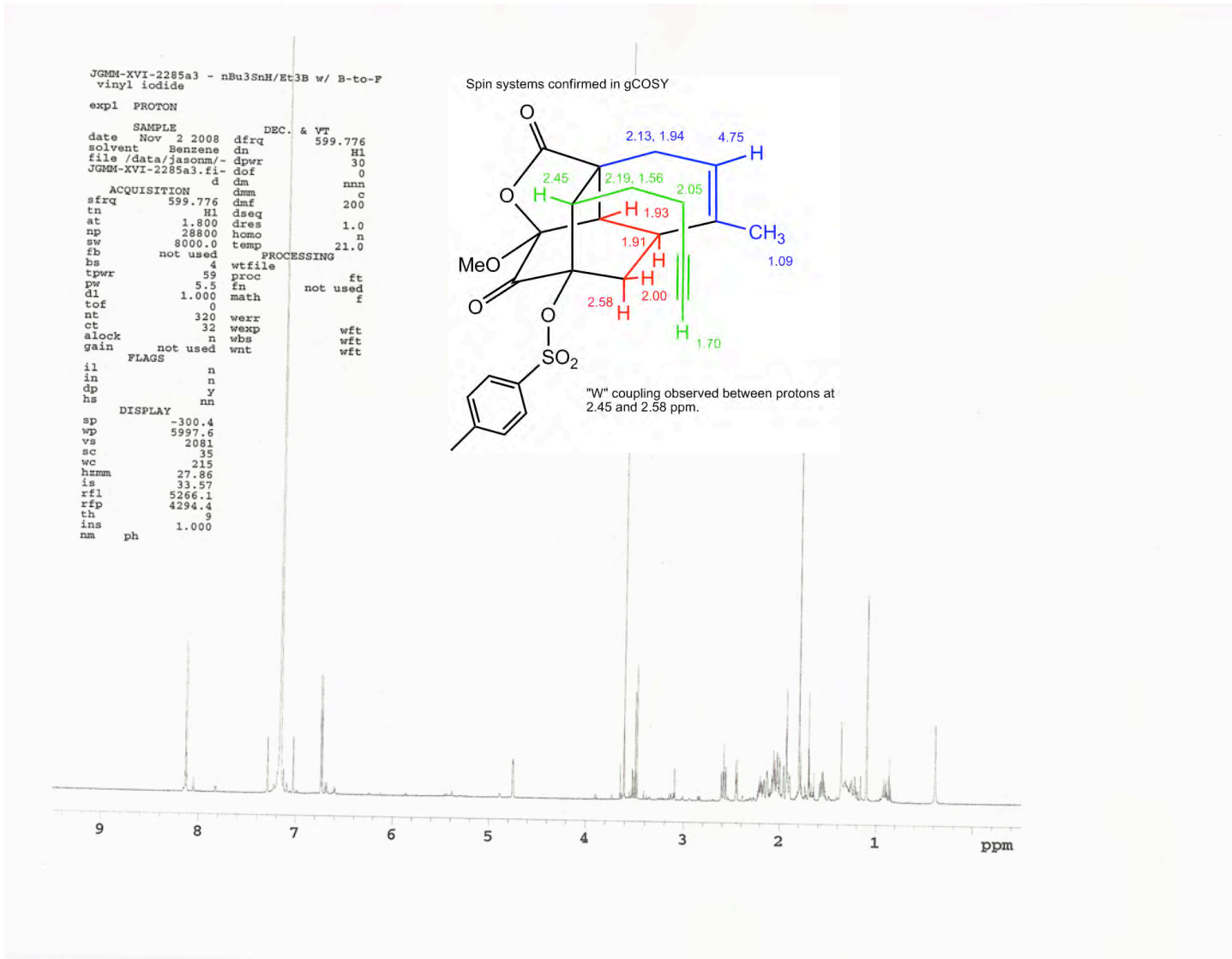
FLAGS	
il	n
in	n
dp	y
hs	nn

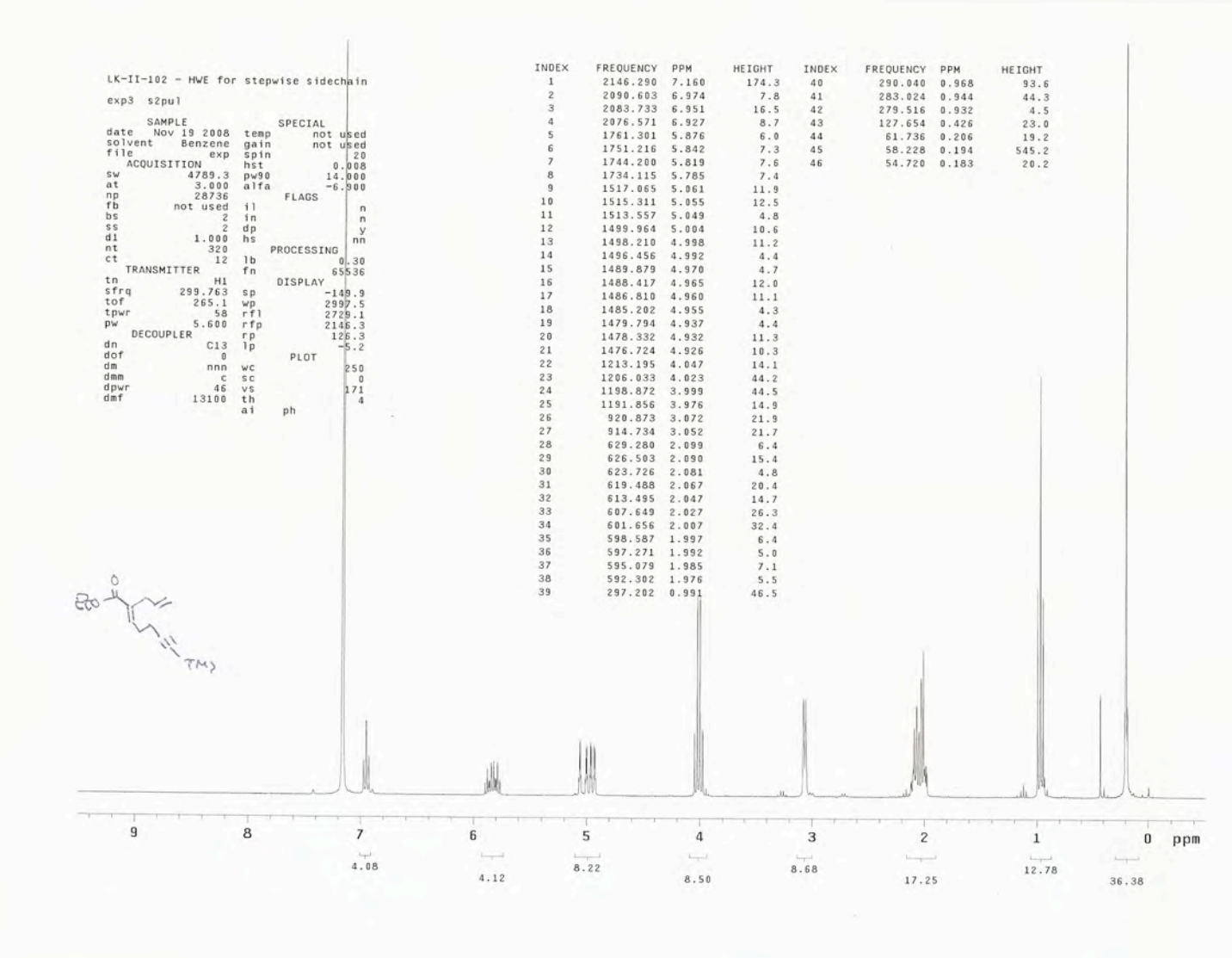
DISPLAY	
sp	-1237.8
wp	28890.9
vs	2034
sc	0
wc	250
hzmm	115.56
is	500.00
rfl	17328.3
rfp	16090.1
th	12
ins	100.000

nm cdc ph

INDEX	FREQUENCY	PPM	HEIGHT
1	24209.651	192.592	13.4
2	21853.328	173.847	19.6
3	18221.196	144.953	25.4
4	17013.278	135.344	16.2
5	16494.843	131.219	36.6
6	16328.644	129.897	38.6
7	16299.989	129.669	89.5
8	16177.874	128.698	88.9
9	16126.736	128.291	134.8
10	16114.392	128.193	1957.8
11	16102.930	128.102	60.7
12	16090.146	128.000	2020.9
13	16077.802	127.902	108.6
14	16065.899	127.807	2034.1
15	13589.225	108.105	21.7
16	12210.258	97.135	25.4
17	11556.924	91.937	28.6
18	10378.983	82.567	24.9
19	8836.903	70.299	52.2
20	6888.804	54.802	46.9
21	6635.758	52.789	31.6
22	6141.129	48.854	38.6
23	5906.158	46.985	34.8
24	4677.079	37.207	30.5
25	4211.104	33.500	48.2
26	3122.655	24.841	40.7
27	2656.680	21.134	41.3
28	2374.098	18.886	45.2




JGMM-XVI-2285a3 - nBu3SnH/Et3B w/ B-to-F
vinyl iodide
expl PROTON
SAMPLE
date Nov 2 2008
solvent Benzene
file /data/jasonm/~
JGMM-XVI-2285a3.fi~
d
ACQUISITION
sfrq 599.776
tn H1
at 1.800
np 28800
sw 8000.0
fb not used
bs 4
tpwr 59
pw 5.5
dl 1.000
tof 0
nt 320
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -300.4
wp 5997.6
vs 2081
sc 35
wc 215
hzmm 27.86
is 33.57
rfl 5266.1
rfp 4294.4
th 9
ins 1.000
nm ph
DEC. & VT
dfrq 599.776
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 21.0
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp wft
wbs wft
wnt wft
Spin systems confirmed in gCOSY
2.13, 1.94
4.75
2.45
2.19, 1.56
2.05
1.93
1.91
2.58
2.00
1.70
1.09
MeO
"W" coupling observed between protons at 2.45 and 2.58 ppm.
9
8
7
6
5
4
3
2
1
ppm


LK-II-102 - HWE for stepwise sidechain
exp3 s2pul
SAMPLE
date Nov 19 2008
solvent Benzene
file exp
ACQUISITION
sw 4789.3
at 3.000
np 28736
fb not used
bs 2
ss 2
dl 1.000
nt 320
ct 12
TRANSMITTER
tn H1
sfrq 299.763
tof 265.1
tpwr 58
pw 5.600
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 46
dmf 13100
SPECIAL
temp not used
gain not used
spin 20
hst 0.008
pw90 14.000
alfa -6.900
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.30
fn 65536
DISPLAY
sp -149.9
wp 2997.5
rfl 2729.1
rfp 2146.3
rp 126.3
lp -5.2
PLOT
wc 250
sc 0
vs 171
th 4
ai ph
INDEX FREQUENCY PPM HEIGHT
1 2146.290 7.160 174.3
2 2090.603 6.974 7.8
3 2083.733 6.951 16.5
4 2076.571 6.927 8.7
5 1761.301 5.876 6.0
6 1751.216 5.842 7.3
7 1744.200 5.819 7.6
8 1734.115 5.785 7.4
9 1517.065 5.061 11.9
10 1515.311 5.055 12.5
11 1513.557 5.049 4.8
12 1499.964 5.004 10.6
13 1498.210 4.998 11.2
14 1496.456 4.992 4.4
15 1489.879 4.970 4.7
16 1488.417 4.965 12.0
17 1486.810 4.960 11.1
18 1485.202 4.955 4.3
19 1479.794 4.937 4.4
20 1478.332 4.932 11.3
21 1476.724 4.926 10.3
22 1213.195 4.047 14.1
23 1206.033 4.023 44.2
24 1198.872 3.999 44.5
25 1191.856 3.976 14.9
26 920.873 3.072 21.9
27 914.734 3.052 21.7
28 629.280 2.099 6.4
29 626.503 2.090 15.4
30 623.726 2.081 4.8
31 619.488 2.067 20.4
32 613.495 2.047 14.7
33 607.649 2.027 26.3
34 601.656 2.007 32.4
35 598.587 1.997 6.4
36 597.271 1.992 5.0
37 595.079 1.985 7.1
38 592.302 1.976 5.5
39 297.202 0.991 46.5
INDEX FREQUENCY PPM HEIGHT
40 290.040 0.968 93.6
41 283.024 0.944 44.3
42 279.516 0.932 4.5
43 127.654 0.426 23.0
44 61.736 0.206 19.2
45 58.228 0.194 545.2
46 54.720 0.183 20.2
TMS
9
8
7
6
5
4
3
2
1
0
ppm
4.08
4.12
8.22
8.50
8.68
17.25
12.78
36.38

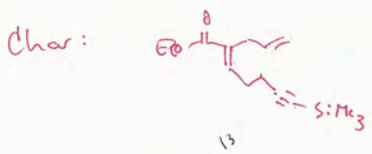
LK-II-102C - HWE, for stepwise chain

exp3 s2pul

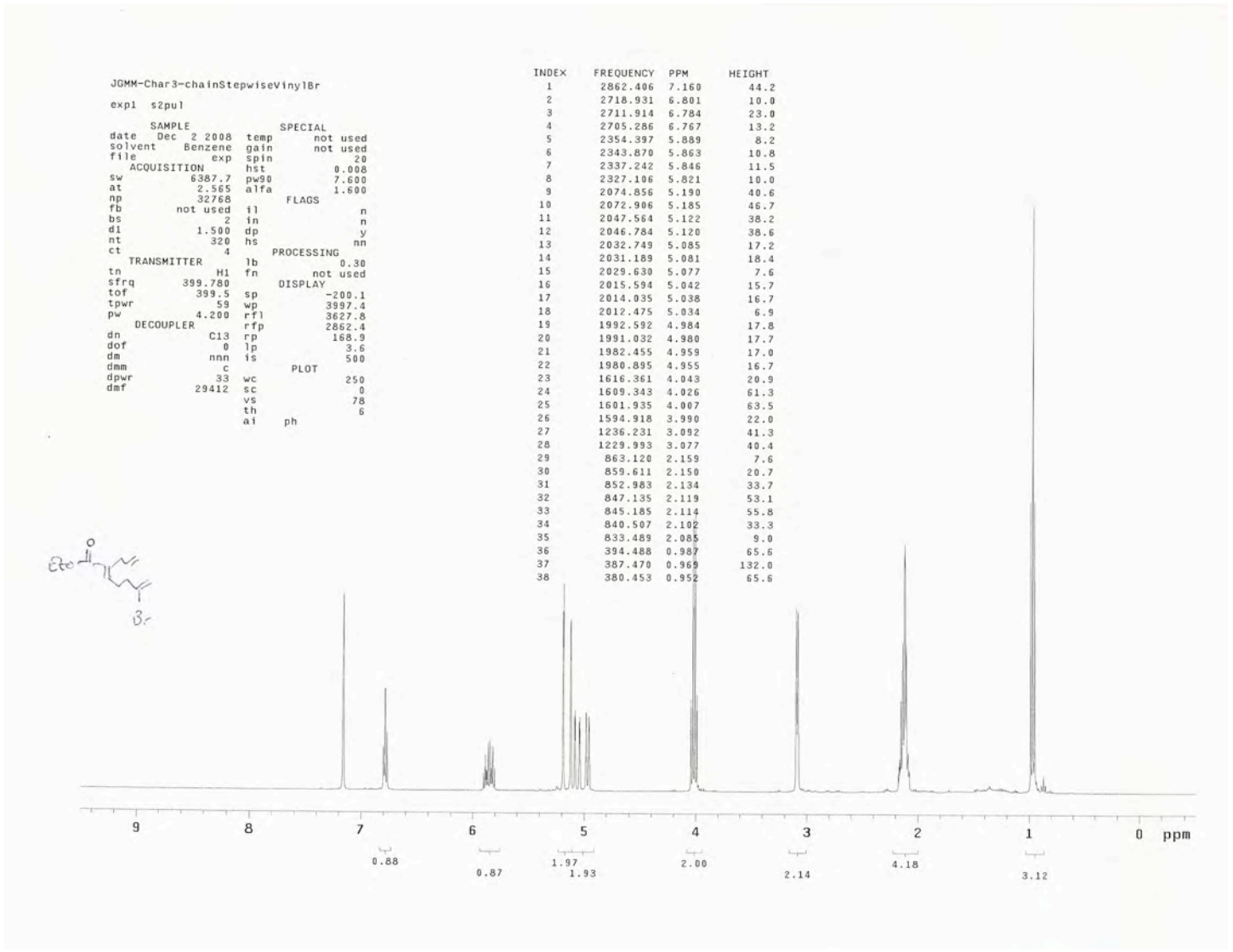
SAMPLE		SPECIAL	
date	Nov 19 2008	temp	not used
solvent	Benzene	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	18797.0	pw90	14.000
at	2.500	alfa	-8.800
np	93984	**FLAGS**	
fb	not used	il	n
bs	4	in	n
di	1.000	dp	y
nt	3200	hs	nn
ct	92	**PROCESSING**	
TRANSMITTER		lb	1.00
tn	C13	fn	131072
sfrq	75.383	**DISPLAY**	
tof	727.6	sp	-1095.8
tpwr	59	wp	18797.0
pw	6.000	rf1	10743.8
DECOUPLER		rfp	9648.0
dn	H1	rp	118.4
dof	0	lp	8.9
dm	yyy	**PLOT**	
dmm	w	wc	250
dpwr	36	sc	0
dmf	7700	vs	130
		th	6
		ai	ph

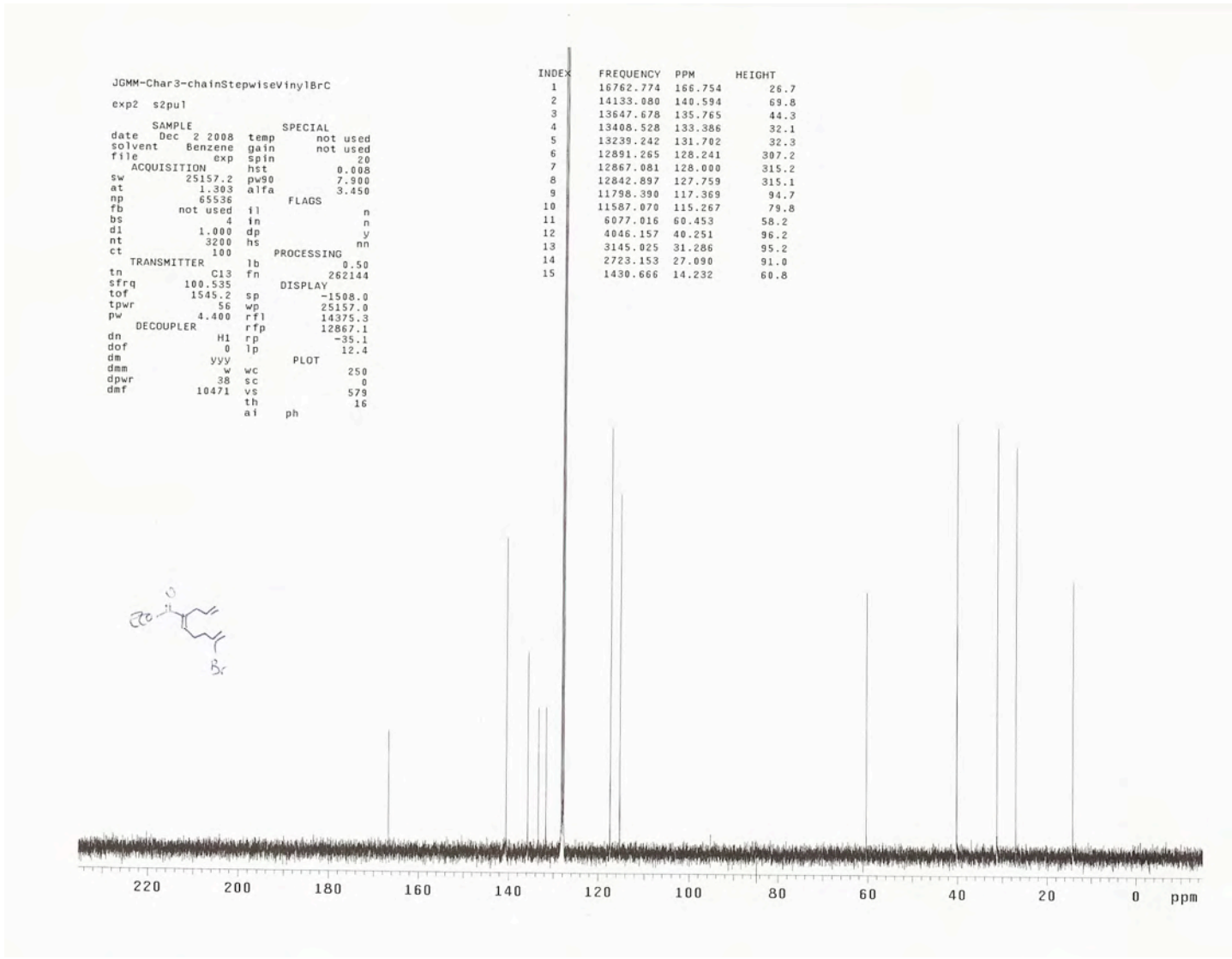
INDEX	FREQUENCY	PPM	HEIGHT
1	12558.972	166.620	12.5
2	10611.152	140.778	49.9
3	10233.692	135.770	38.1
4	9919.046	131.596	25.4
5	9672.091	128.320	84.1
6	9647.998	128.000	84.4
7	9623.905	127.680	83.6
8	8679.968	115.157	52.6
9	8008.513	106.249	20.3
10	6446.471	85.525	12.6
11	4549.419	60.357	41.0
12	2350.055	31.178	64.0
13	2093.061	27.769	80.5
14	1459.181	19.359	71.1
15	1076.271	14.279	60.3
16	12.442	0.165	148.4

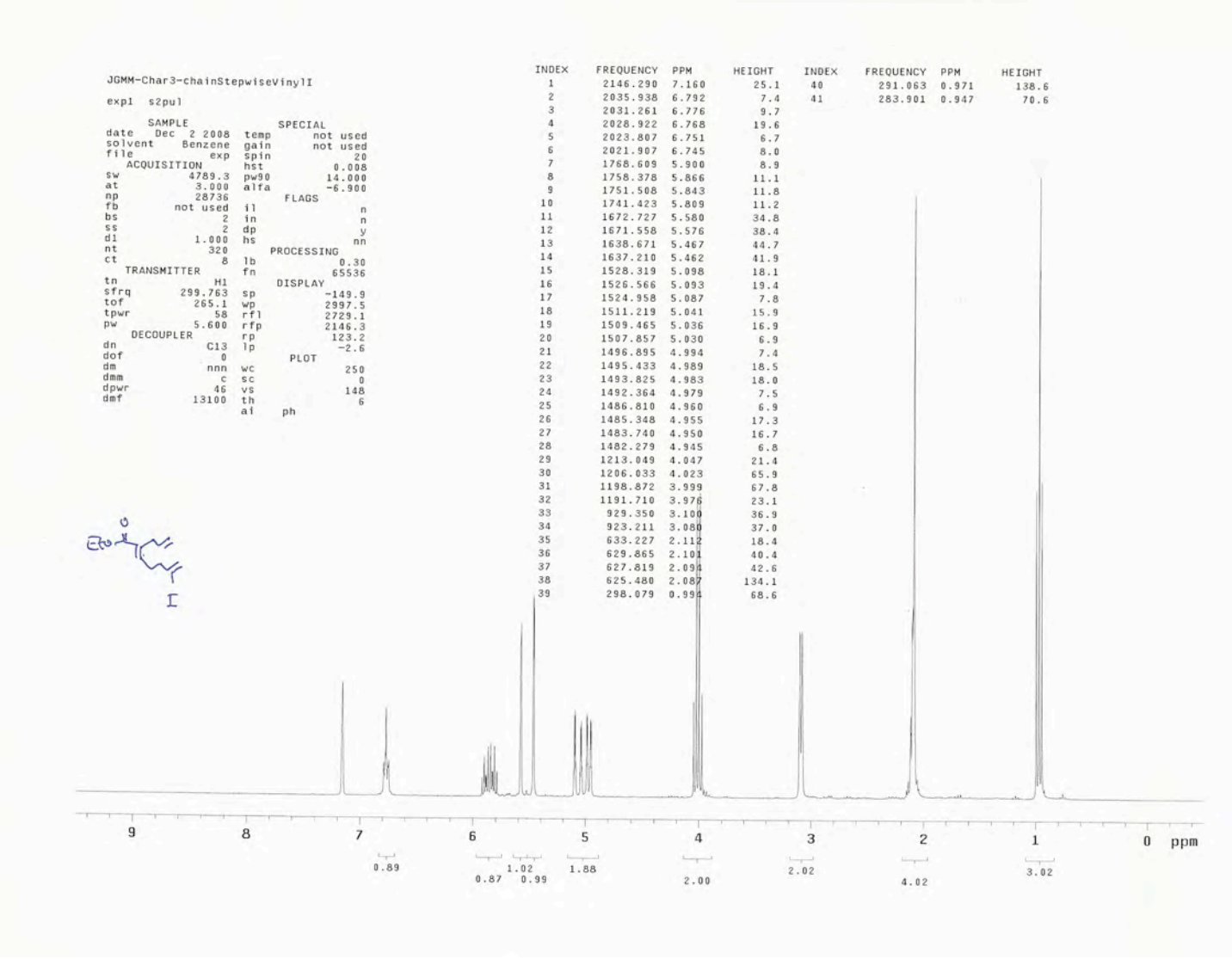
Char:



13


JGMM-Char3-chainStepwiseVinylBr
expl s2pul
SAMPLE
date Dec 2 2008
solvent Benzene
file exp
ACQUISITION
sw 6387.7
at 2.565
np 32768
fb not used
bs 2
di 1.500
nt 320
ct 4
TRANSMITTER
tn H1
sfrq 399.780
tof 399.5
tpwr 59
pw 4.200
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 33
dmf 29412
SPECIAL
temp not used
gain not used
spin 20
hst 0.008
pw90 7.600
alfa 1.600
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.30
fn not used
DISPLAY
sp -200.1
wp 3997.4
rfl 3627.8
rfp 2862.4
rp 168.9
lp 3.6
is 500
PLOT
wc 250
sc 0
vs 78
th 6
ai ph
INDEX FREQUENCY PPM HEIGHT
1 2862.406 7.160 44.2
2 2718.931 6.801 10.0
3 2711.914 6.784 23.0
4 2705.286 6.767 13.2
5 2354.397 5.889 8.2
6 2343.870 5.863 10.8
7 2337.242 5.846 11.5
8 2327.106 5.821 10.0
9 2074.856 5.190 40.6
10 2072.906 5.185 46.7
11 2047.564 5.122 38.2
12 2046.784 5.120 38.6
13 2032.749 5.085 17.2
14 2031.189 5.081 18.4
15 2029.630 5.077 7.6
16 2015.594 5.042 15.7
17 2014.035 5.038 16.7
18 2012.475 5.034 6.9
19 1992.592 4.984 17.8
20 1991.032 4.980 17.7
21 1982.455 4.959 17.0
22 1980.895 4.955 16.7
23 1616.361 4.043 20.9
24 1609.343 4.026 61.3
25 1601.935 4.007 63.5
26 1594.918 3.990 22.0
27 1236.231 3.092 41.3
28 1229.993 3.077 40.4
29 863.120 2.159 7.6
30 859.611 2.150 20.7
31 852.983 2.134 33.7
32 847.135 2.119 53.1
33 845.185 2.114 55.8
34 840.507 2.102 33.3
35 833.489 2.085 9.0
36 394.488 0.987 65.6
37 387.470 0.969 132.0
38 380.453 0.952 65.6
O
EtO
Br
9
8
7
6
5
4
3
2
1
0
ppm
0.88
0.87
1.97
1.93
2.00
2.14
4.18
3.12


JGMM-Char3-chainStepwiseVinylBrC
exp2 s2pul
SAMPLE
date Dec 2 2008
solvent Benzene
file exp
ACQUISITION
sw 25157.2
at 1.303
np 65536
fb not used
bs 4
di 1.000
nt 3200
ct 100
TRANSMITTER
tn C13
sfrq 100.535
tof 1545.2
tpwr 56
pw 4.400
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 10471
SPECIAL
temp not used
gain not used
spin 20
hst 0.008
pw90 7.900
alfa 3.450
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn 262144
DISPLAY
sp -1508.0
wp 25157.0
rfl 14375.3
rfp 12867.1
rp -35.1
lp 12.4
PLOT
wc 250
sc 0
vs 579
th 16
ai ph
INDEX FREQUENCY PPM HEIGHT
1 16762.774 166.754 26.7
2 14133.080 140.594 69.8
3 13647.678 135.765 44.3
4 13408.528 133.386 32.1
5 13239.242 131.702 32.3
6 12891.265 128.241 307.2
7 12867.081 128.000 315.2
8 12842.897 127.759 315.1
9 11798.390 117.369 94.7
10 11587.070 115.267 79.8
11 6077.016 60.453 58.2
12 4046.157 40.251 96.2
13 3145.025 31.286 95.2
14 2723.153 27.090 91.0
15 1430.666 14.232 60.8
O
Br
220
200
180
160
140
120
100
80
60
40
20
0
ppm


JGMM-Char3-chainStepwiseVinylI
expl s2pul
SAMPLE
date Dec 2 2008
solvent Benzene
file exp
ACQUISITION
sw 4789.3
at 3.000
np 28736
fb not used
bs 2
ss 2
d1 1.000
nt 320
ct 8
TRANSMITTER
tn H1
sfrq 299.763
tof 265.1
tpwr 58
pw 5.600
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 46
dmf 13100
SPECIAL
temp not used
gain not used
spin 20
hst 0.008
pw90 14.000
alfa -6.900
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.30
fn 65536
DISPLAY
sp -149.9
wp 2997.5
rfl 2729.1
rfp 2146.3
rp 123.2
lp -2.6
PLOT
wc 250
sc 0
vs 148
th 6
ai ph
INDEX FREQUENCY PPM HEIGHT INDEX FREQUENCY PPM HEIGHT
1 2146.290 7.160 25.1 40 291.063 0.971 138.6
2 2035.938 6.792 7.4 41 283.901 0.947 70.6
3 2031.261 6.776 9.7
4 2028.922 6.768 19.6
5 2023.807 6.751 6.7
6 2021.907 6.745 8.0
7 1768.609 5.900 8.9
8 1758.378 5.866 11.1
9 1751.508 5.843 11.8
10 1741.423 5.809 11.2
11 1672.727 5.580 34.8
12 1671.558 5.576 38.4
13 1638.671 5.467 44.7
14 1637.210 5.462 41.9
15 1528.319 5.098 18.1
16 1526.566 5.093 19.4
17 1524.958 5.087 7.8
18 1511.219 5.041 15.9
19 1509.465 5.036 16.9
20 1507.857 5.030 6.9
21 1496.895 4.994 7.4
22 1495.433 4.989 18.5
23 1493.825 4.983 18.0
24 1492.364 4.979 7.5
25 1486.810 4.960 6.9
26 1485.348 4.955 17.3
27 1483.740 4.950 16.7
28 1482.279 4.945 6.8
29 1213.049 4.047 21.4
30 1206.033 4.023 65.9
31 1198.872 3.999 67.8
32 1191.710 3.976 23.1
33 929.350 3.100 36.9
34 923.211 3.080 37.0
35 633.227 2.112 18.4
36 629.865 2.101 40.4
37 627.819 2.094 42.6
38 625.480 2.087 134.1
39 298.079 0.994 68.6
I
9
8
7
6
5
4
3
2
1
0
ppm
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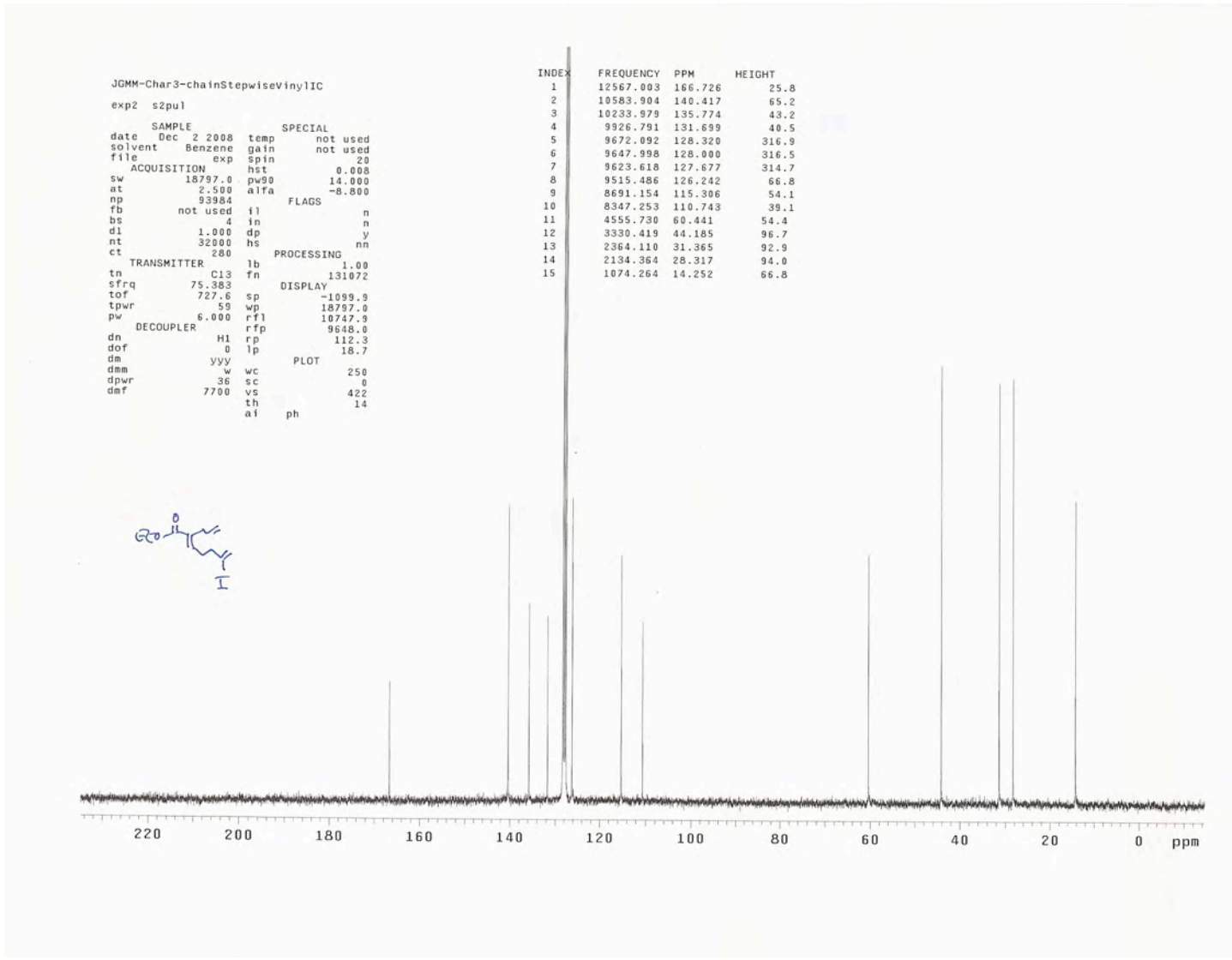
0.87
1.02
0.99
1.88
2.00
2.02
4.02
3.02

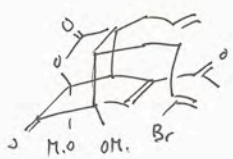

JGMM-Char3-chainStepwiseVinylIC
exp2 s2pul
SAMPLE
date Dec 2 2008
solvent Benzene
file exp
ACQUISITION
sw 18797.0
at 2.500
np 93984
fb not used
bs 4
di 1.000
nt 32000
ct 280
TRANSMITTER
tn C13
sfrq 75.383
tof 727.6
tpwr 59
pw 6.000
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 36
dmf 7700
SPECIAL
temp not used
gain not used
spin 20
hst 0.008
pw90 14.000
alfa -8.800
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn 131072
DISPLAY
sp -1099.9
wp 18797.0
rfl 10747.9
rfp 9648.0
rp 112.3
lp 18.7
PLOT
wc 250
sc 0
vs 422
th 14
ai ph
INDEX FREQUENCY PPM HEIGHT
1 12567.003 166.726 25.8
2 10583.904 140.417 65.2
3 10233.979 135.774 43.2
4 9926.791 131.699 40.5
5 9672.092 128.320 316.9
6 9647.998 128.000 316.5
7 9623.618 127.677 314.7
8 9515.486 126.242 66.8
9 8691.154 115.306 54.1
10 8347.253 110.743 39.1
11 4555.730 60.441 54.4
12 3330.419 44.185 96.7
13 2364.110 31.365 92.9
14 2134.364 28.317 94.0
15 1074.264 14.252 66.8
220
200
180
160
140
120
100
80
60
40
20
0
ppm

JGMM-Char3-stepwiseVinylBr_500

exp3 s2pul

SAMPLE		DEC. & VT	
date	Nov 26 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
JGMM-Char3-stepwis~		dof	0
eVinylBr_500.fid		dm	nnn
ACQUISITION		dmm	c
sfrq	499.920	dmf	200
tn	H1	dseq	
at	1.892	dres	1.0
np	30272	homo	n
sw	8000.0	PROCESSING	
fb	4000	wtfile	
bs	32	proc	ft
tpwr	58	fn	not used
pw	5.5	math	f
d1	2.000		
tof	0	werr	
nt	32	wexp	
ct	32	wbs	
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	342		
sc	35		
wc	215		
hzmm	23.22		
is	33.57		
rfl	5072.8		
rfp	3579.4		
th	3		
ins	3.000		
nm	ph		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3579.408	7.160	341.6	40	861.634	1.724	6.7
2	3220.033	6.441	13.1	41	852.845	1.706	6.5
3	3219.056	6.439	14.8	42	781.556	1.563	161.3
4	3218.080	6.437	14.9	43	607.240	1.215	4.4
5	3217.103	6.435	13.0	44	601.869	1.204	5.8
6	2932.923	5.867	3.5	45	593.080	1.186	5.4
7	2621.888	5.245	9.1	46	587.220	1.175	3.8
8	2620.912	5.243	9.2				
9	2604.798	5.210	8.1				
10	2603.822	5.209	8.0				
11	2592.591	5.186	15.9				
12	2590.638	5.182	49.3				
13	2584.291	5.169	9.2				
14	2258.119	4.517	21.9				
15	2256.166	4.513	19.7				
16	1680.970	3.362	164.8				
17	1677.064	3.355	3.4				
18	1599.916	3.200	134.2				
19	1354.798	2.710	5.2				
20	1348.939	2.698	5.3				
21	1341.127	2.683	5.5				
22	1335.267	2.671	5.2				
23	1252.259	2.505	5.9				
24	1249.818	2.500	6.4				
25	1243.959	2.488	6.4				
26	1241.517	2.483	6.2				
27	1096.009	2.192	6.9				
28	1091.127	2.183	4.7				
29	1086.732	2.174	5.3				
30	1081.361	2.163	5.5				
31	1074.037	2.148	4.8				
32	1067.201	2.135	5.7				
33	1064.759	2.130	5.3				
34	1058.412	2.117	6.2				
35	900.697	1.802	4.5				
36	892.884	1.786	3.4				
37	886.048	1.772	4.9				
38	875.306	1.751	7.3				
39	866.517	1.733	6.9				

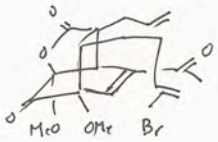


JGMM-Char3-stepwiseVinylBrC

expl s2pul

SAMPLE		DEC. & VT	
date	Nov 26 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	40
	JGMM-Char3-stepwis~	dof	0
	eVinylBr_500C.fid	dm	YYY
ACQUISITION		dmm	W
sfrq	125.717	dmf	13333
tn	C13	dseq	
at	1.300	dres	1.0
np	75146	homo	n
sw	28891.3	PROCESSING	
fb	16000	lb	0.50
bs	4	wtfile	
tpwr	53	proc	ft
pw	6.0	fn	not used
d1	1.500	math	f
tof	1255.5		
nt	32000	werr	
ct	1528	wexp	wft
alock	n	wbs	wft
gain	not used	wnt	
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1237.8		
wp	28890.9		
vs	3033		
sc	0		
wc	250		
hzmm	115.56		
is	500.00		
rf1	17328.3		
rfp	16090.1		
th	10		
ins	100.000		
nm cdc ph			

INDEX	FREQUENCY	PPM	HEIGHT
1	24580.844	195.545	10.8
2	24206.565	192.568	15.7
3	21923.864	174.408	18.6
4	17723.040	140.990	29.7
5	17449.716	138.816	13.3
6	16742.598	133.190	20.7
7	16560.088	131.738	35.5
8	16126.736	128.291	174.1
9	16114.392	128.193	2915.6
10	16102.930	128.102	89.2
11	16090.146	128.000	3008.0
12	16078.684	127.909	105.4
13	16065.899	127.807	3032.6
14	15354.374	122.147	36.5
15	14861.948	118.229	45.4
16	12284.321	97.724	17.8
17	11024.382	87.701	19.1
18	6782.119	53.953	25.9
19	6694.391	53.255	36.6
20	6640.608	52.827	37.5
21	5803.881	46.171	28.2
22	5251.060	41.773	25.9
23	5237.394	41.664	44.9
24	4234.469	33.686	32.0
25	3032.281	24.122	43.9
26	2950.725	23.474	34.3

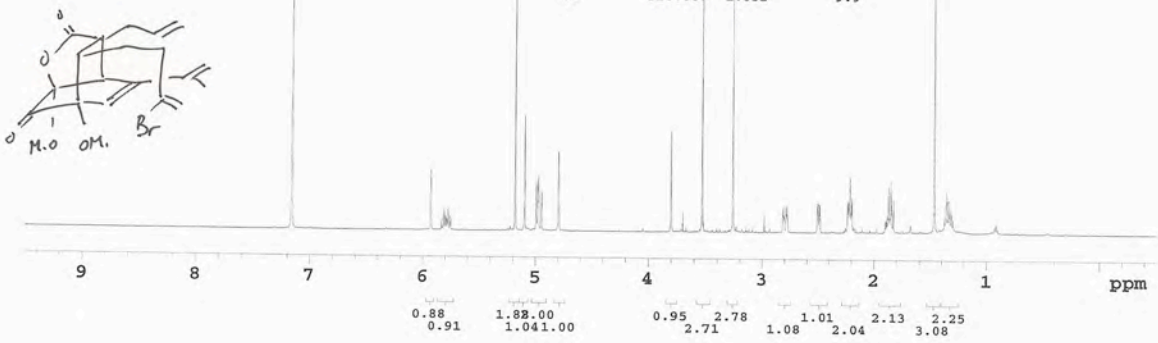


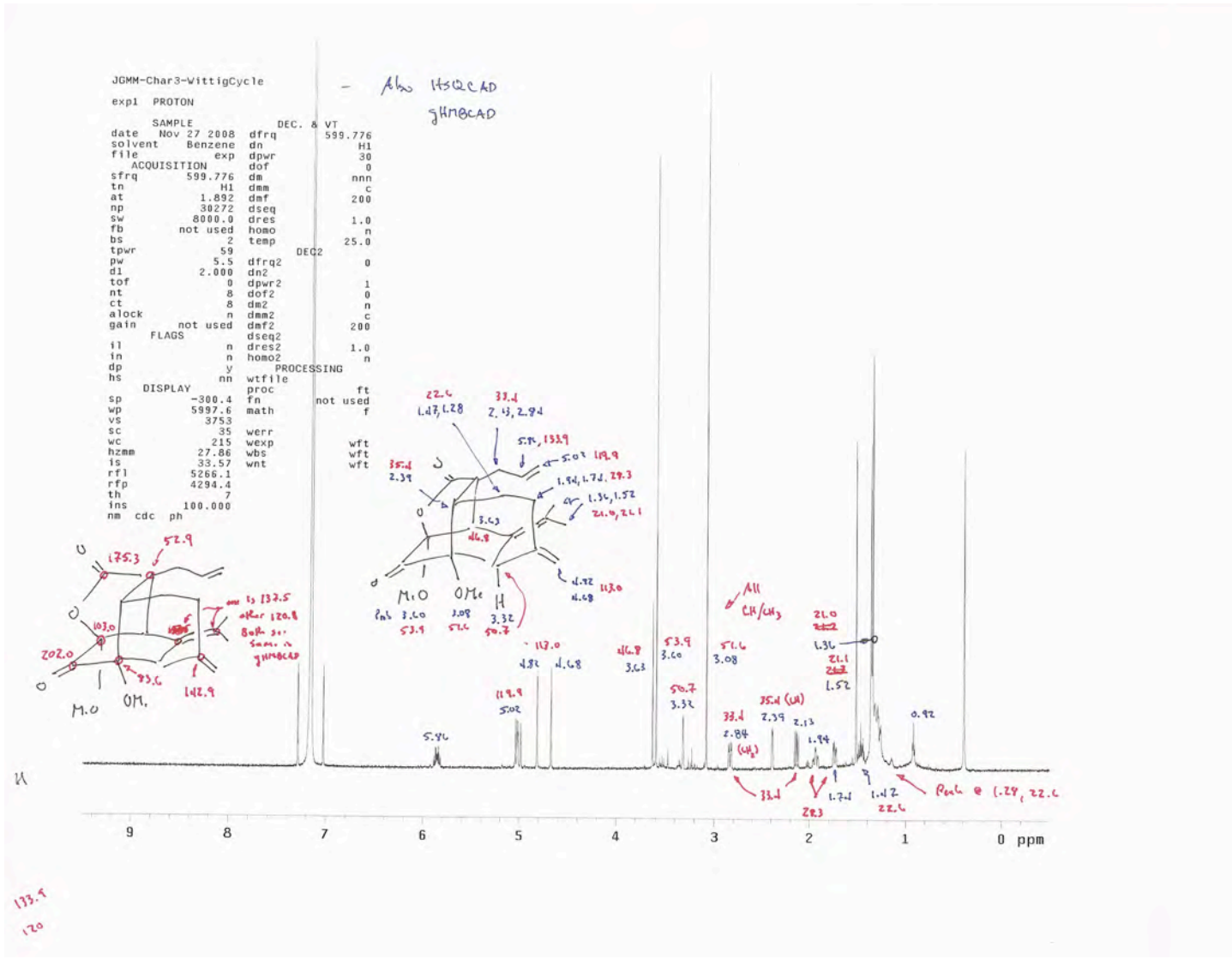
JGMM-Char3-vinylBrWittig3

exp3 s2pul

SAMPLE		DEC. & VT	
date	Nov 27 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
JGMM-Char3-vinylBr~		dof	0
	Wittig3.fid	dm	nnn
ACQUISITION		dmm	c
sfrq	499.920	dmf	200
tn	H1	dseq	
at	1.892	dres	1.0
np	30272	homo	n
sw	8000.0	PROCESSING	
fb	4000	wtfile	
bs	2	proc	ft
tpwr	58	fn	not used
pw	5.5	math	f
d1	2.000		
tof	0	werr	
nt	320	wexp	wft
ct	8	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	151		
sc	35		
wc	215		
hzmm	23.22		
is	33.57		
rfl	5072.8		
rfp	3579.4		
th	4		
ins	2.000		
nm	ph		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3579.408	7.160	66.3	40	922.181	1.845	7.2
2	2964.662	5.930	11.5	41	912.416	1.825	6.4
3	2963.197	5.927	11.6	42	733.216	1.467	61.7
4	2589.173	5.179	60.0	43	680.970	1.362	5.3
5	2546.693	5.094	22.0	44	679.017	1.358	8.0
6	2498.841	4.999	4.7	45	672.669	1.346	7.5
7	2497.377	4.996	9.7	46	671.205	1.343	4.5
8	2495.912	4.993	7.4	47	664.369	1.329	6.5
9	2491.517	4.984	6.7	48	658.509	1.317	4.4
10	2489.564	4.980	9.9				
11	2487.123	4.975	10.5				
12	2485.658	4.972	6.9				
13	2474.427	4.950	5.1				
14	2473.451	4.948	7.9				
15	2471.498	4.944	4.4				
16	2398.255	4.797	15.3				
17	1900.697	3.802	19.1				
18	1898.255	3.797	19.0				
19	1763.490	3.528	151.2				
20	1631.654	3.264	140.3				
21	1406.068	2.813	4.7				
22	1401.673	2.804	4.9				
23	1392.396	2.785	5.2				
24	1388.002	2.776	5.3				
25	1255.677	2.512	5.0				
26	1254.701	2.510	5.3				
27	1252.259	2.505	5.7				
28	1251.283	2.503	5.5				
29	1247.865	2.496	5.5				
30	1246.888	2.494	5.6				
31	1243.959	2.488	5.4				
32	1116.517	2.233	5.9				
33	1113.587	2.228	6.2				
34	1110.658	2.222	6.2				
35	1106.752	2.214	10.9				
36	1101.380	2.203	6.6				
37	1097.962	2.196	6.9				
38	935.365	1.871	8.9				
39	926.087	1.852	9.9				




JGMM-Char3-WittigCycle
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date Nov 27 2008
solvent Benzene
file exp
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tn H1
at 1.892
np 30272
sw 8000.0
fb not used
bs 2
tpwr 59
pw 5.5
d1 2.000
tof 0
nt 8
ct 8
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -300.4
wp 5997.6
vs 3753
sc 35
wc 215
hzmm 27.86
is 33.57
rfl 5266.1
rfp 4294.4
th 7
ins 100.000
nm cdc ph
DEC. & VT
dfrq 599.776
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
PROCESSING
wtfile
proc ft
fn not used
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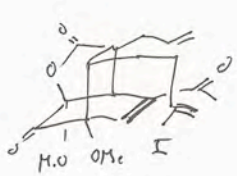
wft
wft
wft
9
8
7
6
5
4
3
2
1
0 ppm

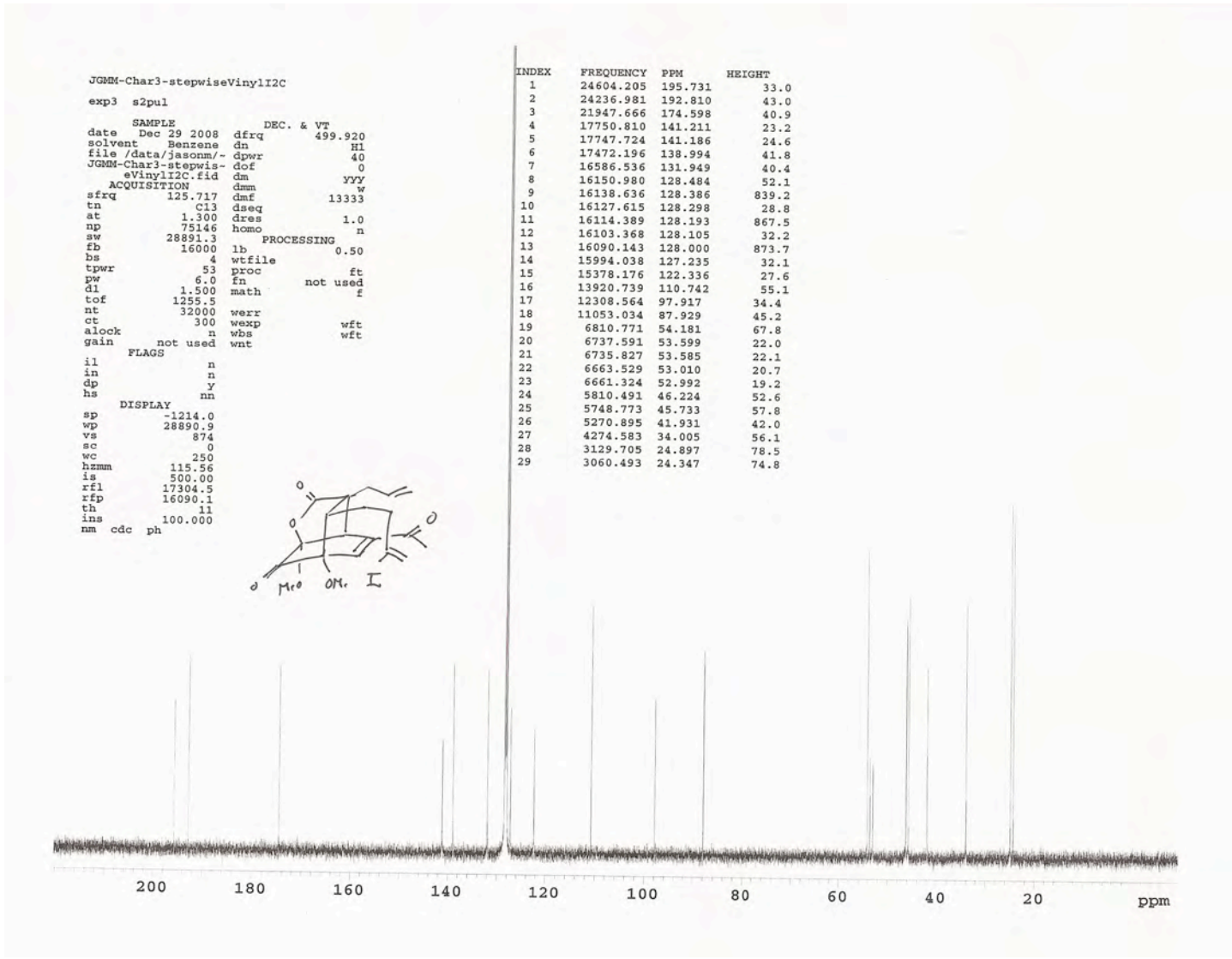
JGMM-Char3-stepwiseVinylI2

exp3 s2pul

SAMPLE		DEC. & VT	
date	Dec 29 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	30
JGMM-Char3-stepwis-		dof	0
eVinylI2.fid		dm	nnn
ACQUISITION		dmm	c
sfrq	499.920	dmf	200
tn	H1	dseq	
at	1.892	dres	1.0
np	30272	homo	n
sw	8000.0	PROCESSING	
fb	4000	wtfile	
bs	4	proc	ft
tpwr	58	fn	not used
pw	5.5	math	f
d1	2.000		
tof	0	werr	
nt	320	wexp	wft
ct	24	wbs	wft
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4999.0		
vs	252		
sc	35		
wc	215		
hzmm	23.22		
is	33.57		
rfl	5072.8		
rfp	3579.4		
th	3		
ins	2.000		
nm	ph		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3579.408	7.160	65.0	40	1248.841	2.498	8.3
2	3234.193	6.469	19.3	41	1246.400	2.493	8.9
3	3233.216	6.468	20.1	42	1240.541	2.481	9.1
4	3231.752	6.465	20.5	43	1238.099	2.477	8.8
5	3230.775	6.463	19.6	44	1087.709	2.176	8.0
6	2952.943	5.907	3.3	45	1083.314	2.167	5.5
7	2949.525	5.900	3.9	46	1082.337	2.165	5.5
8	2948.548	5.898	3.6	47	1078.431	2.157	5.8
9	2944.154	5.889	3.5	48	1073.060	2.146	5.5
10	2942.689	5.886	4.9	49	1059.877	2.120	5.0
11	2941.224	5.883	4.3	50	1053.041	2.106	6.2
12	2939.759	5.880	4.1	51	1051.087	2.103	5.9
13	2935.853	5.873	4.2	52	1044.740	2.090	7.6
14	2933.900	5.869	4.5	53	1036.927	2.074	3.3
15	2932.435	5.866	4.9	54	888.002	1.776	9.4
16	2931.459	5.864	4.0	55	884.095	1.768	4.1
17	2927.064	5.855	3.9	56	879.212	1.759	10.6
18	2925.599	5.852	4.7	57	874.330	1.749	15.2
19	2922.669	5.846	3.8	58	870.912	1.742	4.8
20	2916.810	5.835	3.7	59	869.447	1.739	5.5
21	2809.388	5.620	26.7	60	866.029	1.732	12.9
22	2807.923	5.617	26.2	61	863.099	1.726	5.5
23	2806.459	5.614	12.8	62	859.681	1.720	7.1
24	2727.357	5.456	36.5	63	856.263	1.713	4.1
25	2725.892	5.453	32.5	64	852.845	1.706	3.6
26	2623.353	5.248	12.2	65	791.322	1.583	252.0
27	2622.377	5.246	12.4	66	602.357	1.205	3.3
28	2606.263	5.213	11.2	67	596.986	1.194	3.5
29	2605.287	5.211	11.1	68	593.568	1.187	4.9
30	2595.521	5.192	13.2	69	587.709	1.176	7.2
31	2585.755	5.172	12.4	70	584.779	1.170	4.2
32	2256.654	4.514	32.7	71	582.337	1.165	3.7
33	2254.212	4.509	30.2	72	579.408	1.159	7.1
34	1680.482	3.362	192.8	73	574.037	1.148	4.2
35	1608.705	3.218	205.4	74	570.130	1.140	3.5
36	1362.123	2.725	7.2				
37	1356.263	2.713	7.5				
38	1348.451	2.697	7.9				
39	1342.591	2.686	7.5				



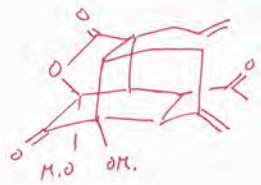

JGMM-Char3-stepwiseVinylI2C
exp3 s2pul
SAMPLE
date Dec 29 2008
solvent Benzene
file /data/jasonm/~
JGMM-Char3-stepwis~
eVinylI2C.fid
ACQUISITION
sfrq 125.717
tn C13
at 1.300
np 75146
sw 28891.3
fb 16000
bs 4
tpwr 53
pw 6.0
d1 1.500
tof 1255.5
nt 32000
ct 300
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1214.0
wp 28890.9
vs 874
sc 0
wc 250
hzmm 115.56
is 500.00
rfl 17304.5
rfp 16090.1
th 11
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.920
dn H1
dpwr 40
dof 0
dm YYY
dmm w
dmf 13333
dseq
dres 1.0
homo n
PROCESSING
lb 0.50
wtfile
proc ft
fn not used
math f
werr
wexp wft
wbs wft
wnt
INDEX FREQUENCY PPM HEIGHT
1 24604.205 195.731 33.0
2 24236.981 192.810 43.0
3 21947.666 174.598 40.9
4 17750.810 141.211 23.2
5 17747.724 141.186 24.6
6 17472.196 138.994 41.8
7 16586.536 131.949 40.4
8 16150.980 128.484 52.1
9 16138.636 128.386 839.2
10 16127.615 128.298 28.8
11 16114.389 128.193 867.5
12 16103.368 128.105 32.2
13 16090.143 128.000 873.7
14 15994.038 127.235 32.1
15 15378.176 122.336 27.6
16 13920.739 110.742 55.1
17 12308.564 97.917 34.4
18 11053.034 87.929 45.2
19 6810.771 54.181 67.8
20 6737.591 53.599 22.0
21 6735.827 53.585 22.1
22 6663.529 53.010 20.7
23 6661.324 52.992 19.2
24 5810.491 46.224 52.6
25 5748.773 45.733 57.8
26 5270.895 41.931 42.0
27 4274.583 34.005 56.1
28 3129.705 24.897 78.5
29 3060.493 24.347 74.8
200
180
160
140
120
100
80
60
40
20
ppm

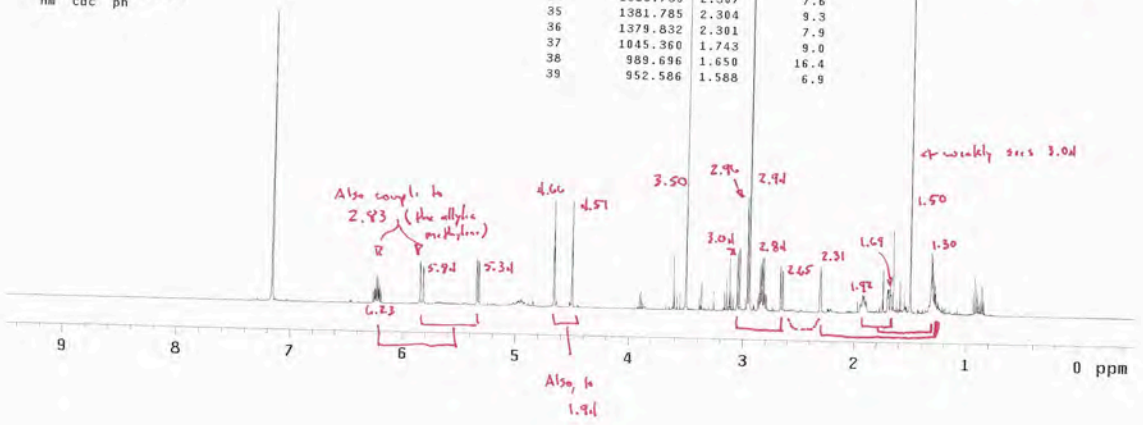
JGMM-XVI-2262c_600 - Proton of nBu3SnH cyclization of vinyl iodide stepwise bicycle

exp1 PROTON

SAMPLE		DEC. & VT	
date	Oct 23 2008	dfrq	599.776
solvent	Benzene	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	599.776	dm	nnn
tn	H1	dmm	c
at	1.892	dmf	200
np	30272	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	DEC2	
tpwr	59	dfrq2	0
pw	5.5	dn2	
d1	1.500	dpwr2	1
tof	0	dof2	0
nt	32	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	PROCESSING	
dp	y	wtfile	
hs	nn	proc	ft
DISPLAY		fn	not used
sp	-300.3	math	f
wp	5997.6		
vs	175	werr	
sc	35	wexp	wft
wc	215	wbs	wft
hzmm	27.86	wnt	wft
is	33.57		
rfl	5266.1		
rfp	4294.4		
th	7		
ins	100.000		
nm cdc ph			

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	4294.871	7.161	55.8	40	897.899	1.497	134.2
2	3508.739	5.850	8.6	41	785.106	1.309	12.3
3	3507.762	5.848	8.6	42	780.711	1.302	11.9
4	3506.297	5.846	8.0	43	778.270	1.298	8.0
5	3491.649	5.822	7.8	44	775.828	1.294	8.4
6	3490.672	5.820	7.3	45	767.039	1.279	6.8
7	3489.207	5.818	7.3	46	552.684	0.921	7.5
8	3205.028	5.344	9.3	47	545.360	0.909	6.8
9	3202.586	5.340	8.8				
10	3194.774	5.327	8.9				
11	3192.332	5.323	8.6				
12	2798.778	4.666	12.0				
13	2796.824	4.663	20.9				
14	2794.871	4.660	11.8				
15	2703.563	4.508	12.0				
16	2701.610	4.504	20.9				
17	2699.656	4.501	11.4				
18	2165.477	3.610	10.7				
19	2100.535	3.502	174.8				
20	1869.578	3.117	10.8				
21	1830.516	3.052	11.0				
22	1829.051	3.050	11.6				
23	1818.309	3.032	12.1				
24	1817.332	3.030	12.6				
25	1776.317	2.962	22.0				
26	1774.852	2.959	22.2				
27	1764.598	2.942	163.1				
28	1707.469	2.847	9.5				
29	1701.121	2.836	9.8				
30	1697.215	2.830	10.7				
31	1689.891	2.818	10.9				
32	1596.629	2.662	9.4				
33	1584.910	2.643	8.3				
34	1383.739	2.307	7.6				
35	1381.785	2.304	9.3				
36	1379.832	2.301	7.9				
37	1045.360	1.743	9.0				
38	989.696	1.650	16.4				
39	952.586	1.588	6.9				



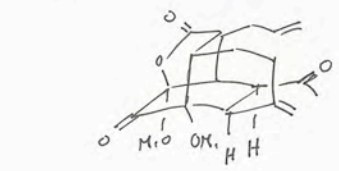


JGMM-XVI-2262cC - nBu3SnH cyclization of stepwise bicycle

exp3 s2pul

SAMPLE		DEC. & VT	
date	Oct 23 2008	dfrq	499.920
solvent	Benzene	dn	H1
file	/data/jasonm/~	dpwr	40
	JGMM-XVI-2262cC.fi~	dof	0
	d	dm	YYY
ACQUISITION		dmm	w
sfrq	125.717	dmf	13333
tn	C13	dseq	
at	1.301	dres	1.0
np	112720	homo	n
sw	43336.9	temp	20.0
fb	24000	PROCESSING	
bs	4	lb	0.50
tpwr	53	wtfile	
pw	6.0	proc	ft
dl	1.500	fn	not used
tof	1255.5	math	f
nt	3200		
ct	528	werr	
alock	n	wexp	wft
gain	not used	wbs	wft
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-1147.8		
wp	28675.3		
vs	809		
sc	0		
wc	250		
hzmm	114.70		
is	500.00		
rfl	24550.9		
rfp	16090.1		
th	12		
ins	100.000		
nm cdc ph			

INDEX	FREQUENCY	PPM	HEIGHT
1	25826.014	205.451	15.6
2	25492.734	202.799	17.0
3	22089.181	175.723	13.1
4	17878.879	142.230	23.7
5	16734.222	133.124	59.6
6	16127.177	128.295	48.4
7	16114.613	128.195	783.7
8	16102.710	128.100	27.0
9	16090.146	128.000	809.5
10	16078.904	127.911	31.4
11	16066.340	127.811	803.7
12	15292.655	121.656	44.2
13	14555.340	115.790	43.3
14	12925.972	102.828	27.5
15	10403.230	82.760	22.4
16	6784.764	53.974	47.7
17	6553.981	52.138	27.3
18	6491.822	51.644	57.0
19	6077.867	48.351	48.1
20	5620.269	44.710	52.2
21	5245.329	41.728	42.2
22	4436.597	35.294	32.5
23	4199.201	33.405	59.1
24	3818.310	30.375	39.7
25	3471.144	27.614	60.1
26	2708.700	21.548	44.3



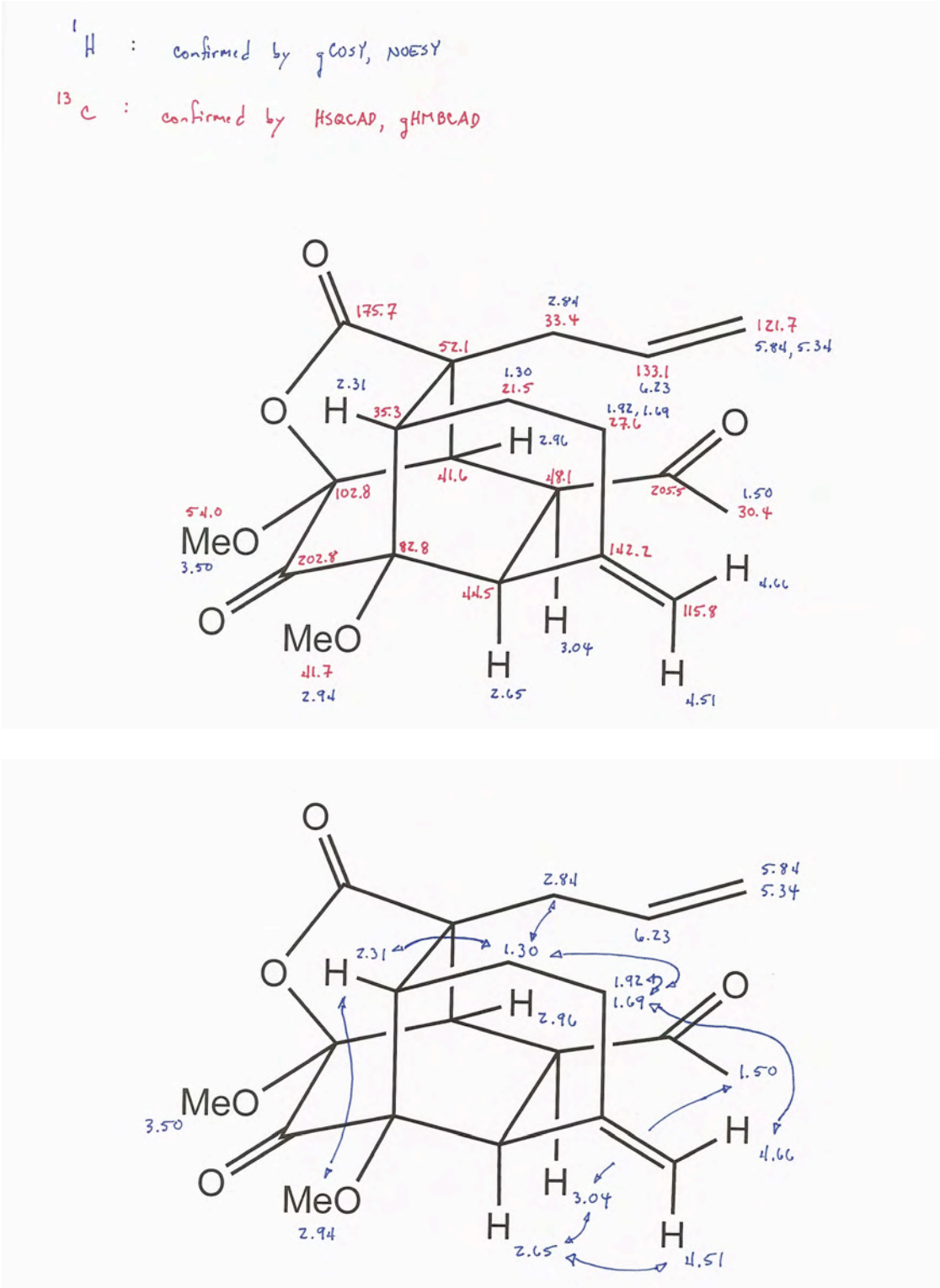


Figure A4.1. ^{1}H and ^{13}C shifts and NOESY correlations for compound **4.40**.

A4.3 Crystal Structure Data for Bicycle 4.36

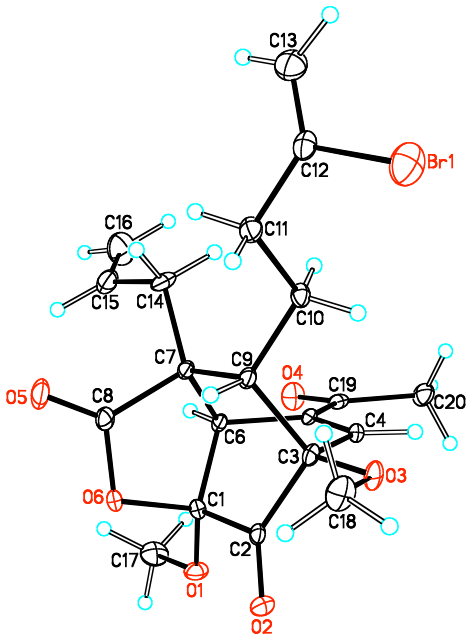


Figure A4.2. ORTEP diagram of **4.36**.

Table A4.1. Crystal data and structure refinement for **4.36**.

Empirical formula	C20 H23 Br O6	
Formula weight	439.29	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.8403(4) Å	a = 111.917(3)°
	b = 10.8899(7) Å	b = 93.099(4)°
	c = 14.4402(9) Å	g = 103.583(3)°
Volume	957.95(10) $Å^3$	
Z	2	
Density (calculated)	1.523 Mg/m^3	
Absorption coefficient	2.180 mm^{-1}	
F(000)	452	

Table A4.1 (Continued)

Crystal size	0.40 x 0.15 x 0.02 mm^3
Theta range for data collection	2.96 to 26.37°.
Index ranges	-8<=h<=8, -13<=k<=13, -18<=l<=18
Reflections collected	22233
Independent reflections	3915 [R(int) = 0.0480]
Completeness to theta = 26.37°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9577 and 0.4760
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3915 / 0 / 247
Goodness-of-fit on F^2	1.120
Final R indices [I>2sigma(I)]	R1 = 0.0568, wR2 = 0.1578
R indices (all data)	R1 = 0.0703, wR2 = 0.1641
Largest diff. peak and hole	0.538 and -0.835 e.$Å^{-3}$

Table A4.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4.36**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-3138(1)	-539(1)	3728(1)	38(1)
O(1)	6532(4)	5470(2)	2501(2)	17(1)
O(2)	6840(4)	4074(2)	3725(2)	18(1)
O(3)	3301(4)	3149(2)	4415(2)	18(1)
O(4)	1450(4)	6675(3)	2452(2)	23(1)
O(5)	3328(4)	1125(3)	437(2)	23(1)
O(6)	5321(3)	3135(2)	1523(2)	15(1)
C(1)	5021(5)	4320(3)	2360(2)	13(1)
C(2)	5249(5)	3970(3)	3289(2)	12(1)
C(3)	3137(5)	3440(3)	3557(2)	13(1)
C(4)	2271(5)	4641(3)	3790(2)	13(1)

Table A4.2 (Continued)

C(5)	2076(5)	5071(3)	3059(2)	12(1)
C(6)	2800(5)	4279(3)	2109(2)	11(1)
C(7)	1839(5)	2711(3)	1692(2)	12(1)
C(8)	3486(5)	2191(3)	1117(2)	15(1)
C(9)	1790(5)	2227(3)	2593(2)	13(1)
C(10)	-318(5)	1701(3)	2843(3)	15(1)
C(11)	-1306(6)	178(4)	2211(3)	20(1)
C(12)	-3322(6)	-361(3)	2470(3)	20(1)
C(13)	-5090(7)	-723(4)	1928(3)	30(1)
C(14)	-155(5)	2205(3)	966(3)	17(1)
C(15)	23(6)	2655(4)	106(3)	21(1)
C(16)	-1061(7)	3331(5)	-133(3)	34(1)
C(17)	6420(6)	6031(4)	1749(3)	24(1)
C(18)	3935(6)	1951(4)	4300(3)	25(1)
C(19)	1385(5)	6293(3)	3143(3)	15(1)
C(20)	639(6)	7035(4)	4092(3)	20(1)

Table A4.3. Bond lengths [Å] and angles [°] for **4.36**.

Br(1)-C(12)	1.897(4)
O(1)-C(1)	1.362(4)
O(1)-C(17)	1.438(5)
O(2)-C(2)	1.187(4)
O(3)-C(3)	1.394(4)
O(3)-C(18)	1.425(5)
O(4)-C(19)	1.215(5)
O(5)-C(8)	1.184(4)
O(6)-C(8)	1.357(4)
O(6)-C(1)	1.467(4)
C(1)-C(6)	1.529(5)
C(1)-C(2)	1.535(5)

Table A4.3 (Continued)

C(2)-C(3)	1.551(5)
C(3)-C(4)	1.494(5)
C(3)-C(9)	1.564(4)
C(4)-C(5)	1.317(5)
C(5)-C(19)	1.480(5)
C(5)-C(6)	1.504(4)
C(6)-C(7)	1.541(4)
C(7)-C(8)	1.526(5)
C(7)-C(14)	1.525(5)
C(7)-C(9)	1.574(5)
C(9)-C(10)	1.536(5)
C(10)-C(11)	1.522(4)
C(11)-C(12)	1.492(5)
C(12)-C(13)	1.294(6)
C(14)-C(15)	1.496(5)
C(15)-C(16)	1.276(6)
C(19)-C(20)	1.495(5)

C(1)-O(1)-C(17)	116.1(3)
C(3)-O(3)-C(18)	116.2(3)
C(8)-O(6)-C(1)	108.3(2)
O(1)-C(1)-O(6)	109.6(3)
O(1)-C(1)-C(6)	119.7(3)
O(6)-C(1)-C(6)	104.6(2)
O(1)-C(1)-C(2)	108.7(3)
O(6)-C(1)-C(2)	104.4(3)
C(6)-C(1)-C(2)	108.8(3)
O(2)-C(2)-C(1)	123.8(3)
O(2)-C(2)-C(3)	125.2(3)
C(1)-C(2)-C(3)	111.0(3)
O(3)-C(3)-C(4)	108.7(3)
O(3)-C(3)-C(2)	112.2(3)
C(4)-C(3)-C(2)	102.9(3)

Table A4.3 (Continued)

O(3)-C(3)-C(9)	115.2(3)
C(4)-C(3)-C(9)	108.3(3)
C(2)-C(3)-C(9)	108.8(3)
C(5)-C(4)-C(3)	116.2(3)
C(4)-C(5)-C(19)	125.4(3)
C(4)-C(5)-C(6)	114.3(3)
C(19)-C(5)-C(6)	120.1(3)
C(5)-C(6)-C(1)	109.3(3)
C(5)-C(6)-C(7)	113.8(3)
C(1)-C(6)-C(7)	99.1(3)
C(8)-C(7)-C(14)	109.6(3)
C(8)-C(7)-C(6)	100.8(3)
C(14)-C(7)-C(6)	114.2(3)
C(8)-C(7)-C(9)	105.8(3)
C(14)-C(7)-C(9)	115.8(3)
C(6)-C(7)-C(9)	109.3(2)
O(5)-C(8)-O(6)	121.4(3)
O(5)-C(8)-C(7)	128.8(3)
O(6)-C(8)-C(7)	109.8(3)
C(10)-C(9)-C(3)	109.5(3)
C(10)-C(9)-C(7)	116.7(3)
C(3)-C(9)-C(7)	108.4(3)
C(11)-C(10)-C(9)	113.0(3)
C(12)-C(11)-C(10)	113.7(3)
C(13)-C(12)-C(11)	127.0(4)
C(13)-C(12)-Br(1)	119.4(3)
C(11)-C(12)-Br(1)	113.6(3)
C(15)-C(14)-C(7)	113.0(3)
C(16)-C(15)-C(14)	125.9(4)
O(4)-C(19)-C(5)	119.9(3)
O(4)-C(19)-C(20)	121.7(3)
C(5)-C(19)-C(20)	118.4(3)

Table A4.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4.36**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	53(1)	32(1)	29(1)	16(1)	7(1)	8(1)
O(1)	13(1)	20(1)	17(1)	9(1)	0(1)	-2(1)
O(2)	14(1)	21(1)	15(1)	5(1)	-2(1)	4(1)
O(3)	26(1)	22(1)	9(1)	9(1)	4(1)	10(1)
O(4)	31(1)	23(1)	22(1)	13(1)	6(1)	12(1)
O(5)	29(1)	20(1)	14(1)	0(1)	7(1)	8(1)
O(6)	14(1)	18(1)	11(1)	2(1)	5(1)	5(1)
C(1)	12(2)	15(1)	11(1)	4(1)	4(1)	4(1)
C(2)	14(2)	12(1)	9(1)	1(1)	3(1)	5(1)
C(3)	16(2)	14(1)	8(1)	4(1)	1(1)	3(1)
C(4)	12(1)	15(2)	9(1)	1(1)	3(1)	4(1)
C(5)	10(1)	10(1)	9(1)	-2(1)	1(1)	1(1)
C(6)	12(1)	10(1)	8(1)	2(1)	1(1)	3(1)
C(7)	13(2)	10(1)	9(1)	2(1)	2(1)	1(1)
C(8)	18(2)	19(2)	10(1)	7(1)	3(1)	6(1)
C(9)	14(2)	11(1)	9(1)	2(1)	2(1)	4(1)
C(10)	19(2)	11(1)	14(2)	3(1)	6(1)	3(1)
C(11)	21(2)	14(2)	19(2)	2(1)	7(1)	-1(1)
C(12)	28(2)	12(2)	16(2)	5(1)	6(1)	1(1)
C(13)	32(2)	25(2)	29(2)	11(2)	4(2)	1(2)
C(14)	16(2)	15(2)	14(2)	5(1)	-5(1)	-3(1)
C(15)	24(2)	21(2)	13(2)	3(1)	1(1)	3(1)
C(16)	40(2)	44(2)	26(2)	21(2)	8(2)	15(2)
C(17)	22(2)	21(2)	29(2)	14(1)	4(2)	0(1)
C(18)	35(2)	25(2)	21(2)	14(1)	3(2)	13(2)
C(19)	10(2)	15(2)	14(2)	3(1)	-2(1)	1(1)
C(20)	21(2)	16(2)	17(2)	0(1)	1(1)	7(1)

Table A4.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for **4.36**.

	x	y	z	U(eq)
H(4A)	1883	5070	4429	16
H(6A)	2627	4647	1579	13
H(9A)	2449	1458	2416	15
H(10A)	-181	1860	3567	18
H(10B)	-1220	2239	2728	18
H(11A)	-1484	27	1488	24
H(11B)	-377	-354	2306	24
H(13A)	-5193	-657	1290	36
H(13B)	-6284	-1054	2167	36
H(14A)	-609	1187	692	21
H(14B)	-1210	2555	1344	21
H(15A)	1034	2416	-299	26
H(16A)	-2091	3592	250	41
H(16B)	-838	3572	-694	41
H(17A)	6105	5283	1074	36
H(17B)	7731	6684	1813	36
H(17C)	5349	6507	1846	36
H(18A)	2796	1128	3940	37
H(18B)	4377	1983	4968	37
H(18C)	5070	1916	3913	37
H(20A)	229	7814	4040	30
H(20B)	1730	7374	4668	30
H(20C)	-533	6404	4190	30